

Lecture Notes in Statistical Mechanics and Mesoscopics

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These are the lecture notes for quantum and statistical mechanics courses that are given by DC at Ben-Gurion University. They are complementary to *Lecture Notes in Quantum Mechanics* [arXiv: quant-ph/0605180]. Some additional topics are covered, including: introduction to master equations; non-equilibrium processes; fluctuation theorems; linear response theory; adiabatic transport; the Kubo formalism; and the scattering approach to mesoscopics. *This is a first draft. Typos are likely.*

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The canonical formalism

[1] The statistical picture of Mechanics

===== [1.1] Random variables

Here is a list of topics that should be covered by a course in probability theory:

- Random variable/observation \hat{x}
- Distribution function $\rho(x)$
- for discrete spectrum $\rho(x) \equiv \text{Prob}(\hat{x} = x)$
- for continuous spectrum $\rho(x)dx \equiv \text{Prob}(x < \hat{x} < x + dx)$
- Changing variables $\hat{y} = f(\hat{x})$, $\tilde{\rho}(y)dy = \rho(x)dx$
- Expectation values $\langle \hat{x} \rangle \equiv \sum_x \rho(x)x$, and more generally $\langle \hat{A} \rangle \equiv \sum_x \rho(x)A(x)$
- Variance $\text{Var}(\hat{x}) = \langle (\hat{x} - \langle \hat{x} \rangle)^2 \rangle = \langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2$
- Moment generating function $Z(\lambda) = \langle e^{\lambda \hat{x}} \rangle$
- Cumulant generating function $g(\lambda)$ is defined through $Z(\lambda) \equiv \exp[g(\lambda)]$
- Gaussian distribution $\rho(x) \propto \exp[\frac{1}{2}((x - \mu)/\sigma)^2]$, $g(\lambda) = \mu\lambda + \frac{1}{2}\sigma^2\lambda^2$
- Joint Distribution function of two variables $\rho(x, y)$
- Correlation function $C_{xy} = \langle \hat{x}\hat{y} \rangle$
- Adding independent random variables:
 - $\hat{S} = \hat{x} + \hat{y}$ (1)
 - $\langle \hat{S} \rangle = \langle \hat{x} \rangle + \langle \hat{y} \rangle$ (2)
 - $\text{Var}(\hat{S}) = \text{Var}(\hat{x}) + \text{Var}(\hat{y})$ (3)
 - $g_s(\lambda) = g_x(\lambda) + g_y(\lambda)$ (4)
- Central limit theorem.
- Remark on quantum postulates [see arXiv: quant-ph/0605180]

===== [1.2] Statistical description of a classical particle

The statistical state of a classical particle is described by a probability function:

$$\rho(x, p) \frac{dx dp}{2\pi} \equiv \text{PROB}(x < \hat{x} < x + dx, p < \hat{p} < p + dp) \quad (5)$$

where the normalization is

$$\iint \frac{dx dp}{2\pi} \rho(x, p) = 1 \quad (6)$$

Expectation values of observables are defined in the usual way:

$$\langle A \rangle = \iint \frac{dx dp}{2\pi} \rho(x, p) A(x, p) \quad (7)$$

We note that in the quantum context one can define a quasi distribution that corresponds to $\rho(x, p)$, known as the *Wigner function*. Furthermore with any observable \hat{A} we can associate a phase space function $A(x, p)$ such that the expectation value can be calculated using classical look-alike formulas. This is known as the *Wigner-Weyl formalism*. This formalism can be regarded as generalization of WKB: Roughly speaking one may say that each Planck cell in phase space can be regarded as representing a quantum state. The volume of Planck cell is $(2\pi\hbar)^d$ where d is the number of freedoms. Above we have assumed $d = 1$. Note that the normalization convention allows a sloppy interpretation of $\rho(x, p)$ as the probability to occupy a Planck cell in phase space. we also remark that the quantum requirement $\text{trace}(\rho^2) \leq 1$ implies that a wavepacket in space space cannot occupy a volume that is less than a Planck cell. The probability function of x is

$$\rho(x) = \int \frac{dp}{2\pi} \rho(x, p) \quad (8)$$

The "spreading" of a wavepacket is characterize by

$$\sigma_x^2 \equiv \text{Var}(\hat{x}) = \langle (\hat{x} - \langle \hat{x} \rangle)^2 \rangle = \langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2 \quad (9)$$

$$\sigma_p^2 \equiv \text{Var}(\hat{p}) = \langle (\hat{p} - \langle \hat{p} \rangle)^2 \rangle = \langle \hat{p}^2 \rangle - \langle \hat{p} \rangle^2 \quad (10)$$

In the quantum context $\sigma_x \sigma_y > (\hbar/2)$. The "energy" of the system is defined as follows:

$$E = \langle \mathcal{H}(\hat{x}, \hat{p}) \rangle = \iint \frac{dx dp}{2\pi} \rho(x, p) \mathcal{H}(x, p) \quad (11)$$

Later we shall define some other "spectral" functions that are related to \mathcal{H} . Those can be written as an expectation value of functions of \mathcal{H} .

===== [1.3] Dynamics in phase space

The Hamiltonian of a free particle is

$$\mathcal{H} = \frac{p^2}{2m} \quad (12)$$

Say that at $t = 0$ the particle is at (x_0, p_0) . The equations of motion are

$$\dot{x} = \frac{\partial \mathcal{H}}{\partial p} = \frac{p}{m} \quad (13)$$

$$\dot{p} = -\frac{\partial \mathcal{H}}{\partial x} = 0 \quad (14)$$

The solution is:

$$x(t) = x_0 + \frac{t}{m} p_0 \quad (15)$$

$$p(t) = p_0 \quad (16)$$

There are two points of view with regard to the evolution: (i) Heisenberg: the evolution is of random variables; (ii) Schrodinger: the evolution is of a probability functions. In statistical mechanics we prefer the latter point of view. Evolution takes place in phase space. Liouville theorem applies. Let us see how we use the "Schrodinger picture" in the above example. The free particle has been prepared in a "deterministic preparation" at the point (x_0, p_0) in phase space. Accordingly

$$\rho_{t=0}(x, p) = 2\pi \delta(p - p_0) \delta(x - x_0) \quad (17)$$

After time t the state is

$$\rho_t(x, p) = 2\pi\delta(p - p_0) \delta\left(x - \left(x_0 + \frac{p_0}{m}t\right)\right) \quad (18)$$

Above $\rho_t(x, p)$ is the probability function of the random variables

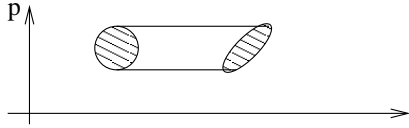
$$\hat{x}_t = \hat{x}_0 + \frac{t}{m}\hat{p}_0 \quad (19)$$

$$\hat{p}_t = \hat{p}_0 \quad (20)$$

If the preparation is not deterministic one observes “spreading”.

$$\sigma_x(t) = \sqrt{\sigma_x^2(0) + \left(\frac{\sigma_p(0)}{m}\right)^2 t^2} \approx \frac{\sigma_p(0)}{m} t \quad (21)$$

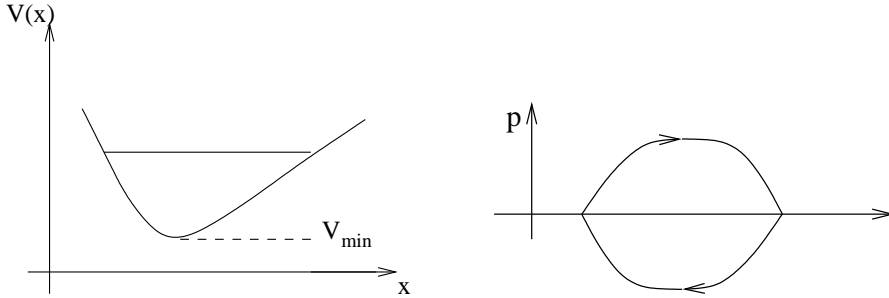
It should be clear that “spreading” is a classical dynamic effect. In quantum mechanics this effect is unavoidable because deterministic preparations are excluded.



More generally we can discuss the spreading of a wavepacket in the case of a non-linear oscillator. The Hamiltonian is

$$\mathcal{H} = \frac{p^2}{2m} + V(x) \quad (22)$$

The energy $V_{\min} < E < \infty$ is a constant of motion. The spreading leads to a quasi-ergodic distribution within an energy shell. It is not really ergodic because if we start with a mono-energetic distribution it will not fill uniformly the energy surface (which is a “circle”).



===== [1.4] The route to ergodicity

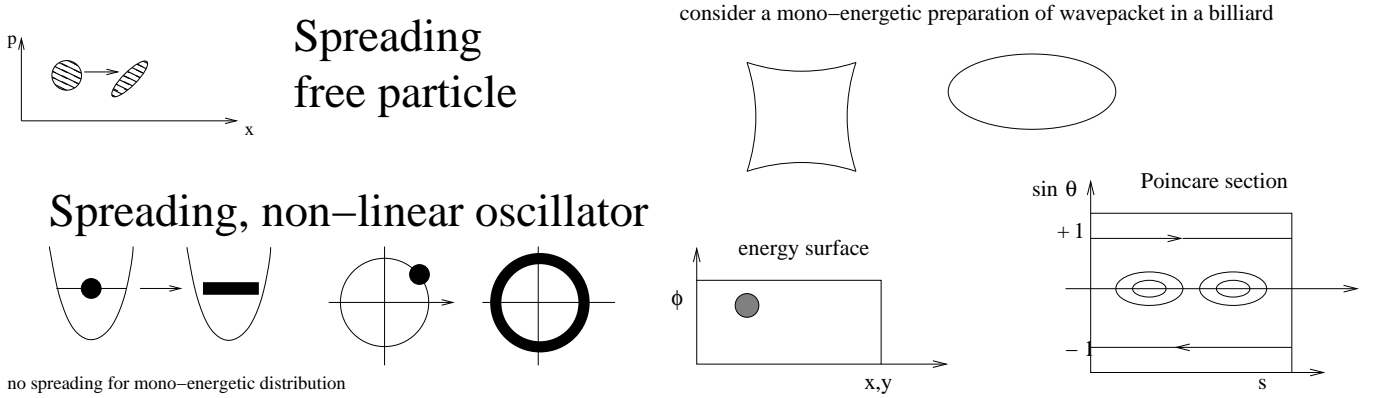
This section will be expanded in future version. It outlines some major observation with regard to the dynamics of classical Hamiltonian systems.

Simple 1D system:— The student is expected to be familiar with the dynamics of harmonic oscillator; potential well; pendulum. In the case of non-linear oscillations we have the *spreading* effect. In the case of a pendulum we have a multi-component phase space with separatrix. The dynamics is not chaotic. One can define the oscillation frequency $\omega(E)$ as a function of energy. In the quantum case $\omega(E)$ corresponds to the level spacing at the vicinity of the energy E .

Chaotic system:— The student is expected to be familiar with the dynamics in simple billiards. The visualization can be achieved using a Poincare section. In the case of a Sinai billiard (motivated by the discussion of Lorentz gas) the dynamics is fully chaotic, leading to ergodization. More generally we might have *mixed phase space* that contains "chaotic sea" as well as "islands".

Ergodization:— The evolution of a chaotic system leads to an ergodization on the energy shell. This can be mathematically described using the Boltzmann approach: coarse graining of phase space by dividing it into cells; definition of Boltzmann entropy. Eventually the system will become stationary-like, as if it were prepared in a state that has maximum entropy.

Driven system:— There is a complicated route to chaos in the case of driven integrable (1D) systems. In contrast to that in the case of driven globally chaotic systems the picture is qualitatively simple: if we prepare the system initially within an energy shell, it will "evolve" with this energy shell, along with diffusion transverse to the energy shell. This diffusion leads in general to increase of the average energy (heating).



===== [1.5] Stationary states

The evolution of a statistical state is determined by the Liouville equation of classical mechanics, which becomes the von-Neumann Liouville equation in quantum mechanics.

$$\frac{\partial \rho}{\partial t} = [\mathcal{H}, \rho]_{\text{PB}} \quad (23)$$

We consider non-driven bounded systems, and focus our attention on *stationary* states that do not change in time. This means $\partial \rho / \partial t = 0$. In the classical language ρ can be regarded as a mixture of "energy shells", while in the quantum language it means that $\rho \mapsto \text{diag}\{p_n\}$ is a mixture of energy eigenstates. In particular the microcanonical state is

$$\rho(x, p) = \frac{1}{g(\mathcal{E})} \delta(\mathcal{H}(x, p) - \mathcal{E}) \quad (24)$$

and the canonical state is

$$\rho(x, p) = \frac{1}{Z(\beta)} e^{-\beta \mathcal{H}(x, p)} \quad (25)$$

where the density of states and the partition function are defined as

$$g(E) = \text{trace}(\delta(E - \mathcal{H})) = \sum_n \delta(E - E_n) \quad (26)$$

$$Z(\beta) = \text{trace}(e^{-\beta \mathcal{H}}) = \sum_n e^{-\beta E_n} = \int g(E) dE e^{-\beta E} \quad (27)$$

It is convenient to write the probability density to find the system at some particular energy E as

$$\rho(E) = \iint \frac{dx dp}{2\pi} \rho(x, p) \delta(E - \mathcal{H}(x, p)) \equiv g(E) f(E) \quad (28)$$

where the respective occupation probability functions are

$$f(E) = \frac{1}{g(E)} \delta(E - \mathcal{E}) \quad [\text{microcanonical}] \quad (29)$$

$$f(E) = \frac{1}{Z(\beta)} e^{-\beta E} \quad [\text{canonical}] \quad (30)$$

If we have a many body system of non-interacting particles we can re-interpret $f(E)$ as the occupation function, and accordingly $\rho(E)$ becomes the energy distribution of the particles (with normalization N).

===== [1.6] The microcanonical and canonical states

Let us assume the following total Hamiltonian for a universe that consists of system and environment:

$$\mathcal{H}_{\text{total}} = \mathcal{H}(Q) + \mathcal{H}_{\text{env}}(Q_\alpha) + \mathcal{H}_{\text{int}}(Q, Q_\alpha) \quad (31)$$

For sake of presentation we do not write the conjugate momenta, so Q stands for (Q, P) or it may represent spin freedoms. If one neglect the interaction the eigenenergies are written as $E_{rR} = E_r + E_R$, where r labels system states and R labels environmental states.

It is argued that the weak interaction with the environment leads after relaxation to a canonical state which is determined by the parameter

$$\beta = \frac{d}{dE} \log(g_{\text{env}}(E)) \quad (32)$$

where $g_{\text{env}}(E)$ is the density of states, which is assumed to be huge and rapidly growing with energy. The argument is based on the assumption that the universe (system+environment) is (say) a closed system with some total energy E_{total} . After ergodization the system get into a stationary-like state that resembles a microcanonical states:

$$p_{r,R} \propto \delta(E_{\text{total}} - (E_r + E_R)) \quad (33)$$

with finite width (broadened) delta function. The probability p_r to find the system in a state E_r is proportional to $g_{\text{env}}(E_{\text{total}} - E_r) \approx g_{\text{env}}(E_{\text{total}}) e^{-\beta E_r}$. Accordingly

$$p_r = \frac{1}{Z} e^{-\beta E_r} \quad (34)$$

where the so-called partition function provides the normalization

$$Z(\beta) = \sum_r e^{-\beta E_r} \quad (35)$$

The partition function may depend on parameters that appear in the system Hamiltonian. Therefore we use in general the notation $Z(\beta, X)$.

===== [1.7] Mathematical digression

Sometimes it is more appropriate to expand the log of a function. Specifically this would be the case if the function is definite positive and span many decades. Let us see what is the error which is involved in such an expansion:

$$f(x) = x^N \quad (36)$$

$$f(x + \delta x) = x^N + Nx^{N-1}\delta x + N^2x^{N-2}\delta x^2 \quad (37)$$

$$\delta x \ll x/N \quad (38)$$

Optionally we expand the log of the function:

$$S(x) \equiv \ln f(x) = N \ln(x) \quad (39)$$

$$S(x + \delta x) = N \ln(x) + \frac{N}{x}\delta x + \frac{N}{x^2}\delta x^2 \quad (40)$$

$$\delta x \ll x \quad (41)$$

Thus we have the recipe:

$$f(x + \delta x) \approx f(x)e^{\beta\delta x} \quad (42)$$

where

$$\beta \equiv \frac{\partial \ln f(x)}{\partial x} \quad (43)$$

In complete analogy we have:

$$g(E_0 + \epsilon) \approx g(E_0)e^{\beta\epsilon} \quad (44)$$

where β is the log derivative of the DOS.

[2] Spectral functions

Various types of spectral functions are defined in mathematical physics. In the quantum context they characterize the spectrum $\{E_n\}$ of energies of as given Hamiltonian \mathcal{H} . In the continuum or classical limit it is essential to define a *measure*. Below we focus on the most popular spectral functions in statistical mechanics: the density of states $g(E)$, and the partition function $Z(\beta)$. We shall see later that the state equations of a system in equilibrium can be derived from, say, the partition function. Hence the spectral function serves as a *generating function*.

In the section below we define $g(E)$ and $Z(\beta)$, and show how they are calculated using standard examples: Two level system; Harmonic oscillator; Particle in a box; Particle with general dispersion relation; The effect of $A(x), V(x)$ potential; Several particles; Identical classical particles, the Gibbs factor; Particles with interactions; In particular two quantum particles; Molecules of type AA and AB (exercise).

===== [2.1] The definition of counting and partition functions

We consider a time independent bounded system which is described by a Hamiltonian \mathcal{H} whose eigenvalues are E_r . We can characterize its energy spectrum by the functions

$$\mathcal{N}(E) \equiv \sum_r \Theta(E - E_r) = \sum_{E_r < E} 1 \quad (45)$$

$$Z(\beta) \equiv \sum_r e^{-\beta E_r} \quad (46)$$

If we have a large system we can smooth $\mathcal{N}(E)$, and then we can define the density of states as

$$g(E) \equiv \frac{d\mathcal{N}(E)}{dE} = \overline{\sum_r \delta(E - E_r)} \quad (47)$$

Note that

$$Z(\beta) = \int g(E) dE e^{-\beta E} \quad (48)$$

For a classical particle in 1D we can use the above definitions with the prescription

$$\sum_r \mapsto \iint \frac{dx dp}{2\pi\hbar} \quad (49)$$

Each "Planck cell" in phase space represents a state. Accordingly

$$\mathcal{N}(E) = \iint \frac{dx dp}{2\pi} \Theta(E - \mathcal{H}(x, p)) = \iint_{\mathcal{H}(x, p) < E} \frac{dx dp}{2\pi} \quad (50)$$

$$Z(\beta) = \iint \frac{dx dp}{2\pi} e^{-\beta \mathcal{H}(x, p)} = \int g(E) dE e^{-\beta E} \quad (51)$$

In what follows the Gaussian integral is useful:

$$\int e^{-\frac{1}{2}ax^2} dx = \left(\frac{2\pi}{a}\right)^{\frac{1}{2}} \quad (52)$$

===== [2.2] Two level system or spin

The Hamiltonian of spin 1/2 in magnetic field is

$$\mathcal{H} = \frac{1}{2}\epsilon\sigma_3 \quad (53)$$

The eigenstates are $|+\rangle$ and $|-\rangle$ with eigenvalues $E_{\pm} = \pm\epsilon/2$. Accordingly

$$Z(\beta) = e^{-\beta(-\frac{\epsilon}{2})} + e^{-\beta(\frac{\epsilon}{2})} = 2 \cosh\left(\frac{1}{2}\epsilon\beta\right) \quad (54)$$

Optionally we can write the energies of any two level system as $E_r = \epsilon n$ with $n = 0, 1$ then

$$Z(\beta) = (1 + e^{-\beta\epsilon}) \quad (55)$$

===== [2.3] Two spins system in interaction

If we have N is interacting spins the sum over states can be factorized and we simply get

$$Z_N(\beta) = \left(Z_1(\beta)\right)^N \quad (56)$$

For two spins in the absence of magnetic field we get $Z_2 = 2^2 = 4$. Let us see what happens if there is an interaction:

$$\mathcal{H} = \epsilon \sigma^a \cdot \sigma^b = (2S^2 - 3) \epsilon \quad (57)$$

where $S = \frac{1}{2}\sigma^a + \frac{1}{2}\sigma^b$. The energy levels are $E_{singlet} = -3\epsilon$ and $E_{triplet} = \epsilon$. Accordingly

$$Z(\beta) = e^{3\beta\epsilon} + 3e^{-\beta\epsilon} \quad (58)$$

===== [2.4] Harmonic oscillator

The Hamiltonian of Harmonic oscillator is

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \quad (59)$$

The eigenstates are $|n\rangle$ with eigenvalues $E_n = \left(\frac{1}{2} + n\right)\omega$. Accordingly

$$Z(\beta) = \sum_{n=0}^{\infty} e^{-\beta(\frac{1}{2}+n)\omega} = \frac{1}{2 \sinh\left(\frac{1}{2}\omega\beta\right)} \quad (60)$$

Note that if we write the energies as $E_r = \omega n$ with $n = 0, 1, 3, 4, \dots$ then

$$Z(\beta) = \frac{1}{1 - e^{-\beta\omega}} \quad (61)$$

Now let us see how the classical calculation is done.

$$\mathcal{N}(E) = \frac{1}{2\pi} \text{ ellipse area} = \frac{1}{2\pi} \pi \left(\frac{2E}{m\omega^2} \right)^{\frac{1}{2}} (2mE)^{\frac{1}{2}} = \frac{E}{\omega} \quad (62)$$

$$Z(\beta) = \int dx e^{-\beta \frac{1}{2} m x^2} \int \frac{dp}{2\pi} e^{-\beta \frac{p^2}{2m}} = \left(\frac{2\pi}{\beta m \omega^2} \right)^{\frac{1}{2}} \left(\frac{m}{2\pi\beta} \right)^{\frac{1}{2}} = \frac{T}{\omega} \quad (63)$$

One can verify the validity of WKB quantization.

===== [2.5] Particle in a 1D box

The simplest is to assume periodic boundary conditions

$$\mathcal{H} = \frac{p^2}{2m} \quad x \in [0, L] \quad (\text{ring}) \quad (64)$$

The eigenstates are the momentum states $|p\rangle$ with

$$p = \frac{2\pi}{L} n \quad \text{where } n = 0, \pm 1, \pm 2, \dots \quad (65)$$

Hence the eigenvalues are

$$E_n = \frac{1}{2m} \left(\frac{2\pi}{L} n \right)^2 \quad (66)$$

The number of states up to energy E is

$$\mathcal{N}(E) = 2 \frac{L}{2\pi} (2mE)^{\frac{1}{2}} \equiv \frac{1}{\pi} k_E L \equiv 2 \frac{L}{\lambda_E} \quad (67)$$

The density of states is

$$g(E) = \frac{L}{\pi v_E} \quad (68)$$

The 1D case here is pathological because in general the density of states grows rapidly with energy. Nevertheless in the limit of "infinite volume" we may treat the spectrum as a continuum:

$$Z(\beta) = \sum_{n=-\infty}^{\infty} e^{-\beta E_n} \approx \int_{-\infty}^{\infty} dn e^{-\beta \frac{1}{2m} \left(\frac{2\pi}{L} \right)^2 n^2} = L \left(\frac{m}{2\pi\beta} \right)^{\frac{1}{2}} \equiv \frac{L}{\lambda_T} \quad (69)$$

Let us see how the calculation is carried out classically. We can still consider a ring, or optionally we can write the Hamiltonian with a box potential $V_L(x)$. Then we get

$$\mathcal{N}(E) = \text{rectangle area} = \frac{1}{2\pi} \times L \times 2 (2mE)^{\frac{1}{2}} = 2 \frac{L}{\lambda_E} \quad (70)$$

$$Z(\beta) = \int dx \int \frac{dp}{2\pi} e^{-\beta \frac{p^2}{2m}} = L \left(\frac{m}{2\pi\beta} \right)^{\frac{1}{2}} = \frac{L}{\lambda_T} \quad (71)$$

One can verify the validity of WKB quantization.

===== [2.6] A particle in 3D box, or higher dimensions

Consider a particle in a $d=3$ box of volume $V = L^d$.

$$\mathcal{H} = \sum_{i=1}^3 \frac{p_i^2}{2m} + [\text{implicit boundary conditions with volume } L^d] \quad (72)$$

The eigenstates are

$$\vec{p} = \frac{2\pi}{L} (n_1, n_2, n_3) \quad (73)$$

$$E_{n_1 n_2 n_3} = \frac{1}{2m} \left(\frac{2\pi}{L} \right)^2 (n_1^2 + n_2^2 + n_3^2) \quad (74)$$

The summation over the states factorizes:

$$Z(\beta) = \sum_{n_1 n_2 n_3} e^{-\beta E_{n_1 n_2 n_3}} = \left(\sum_n e^{-\beta E_n} \right)^3 = \frac{V}{\lambda_T^3} \quad (75)$$

The above calculation is easily generalized to $d > 1$ dimensions. Furthermore, as far as the *classical* calculation is concerned N particles is formally like $d \mapsto Nd$. The counting function is

$$\mathcal{N}(E) = \frac{1}{(2\pi)^d} \frac{\Omega_d}{d} (k_E L)^d = \left\{ \frac{2}{\pi} \right\} \left(\frac{L}{\lambda_E} \right)^d \quad (76)$$

and accordingly

$$g(E) = \frac{\Omega_d}{(2\pi)^d} (k_E L)^{d-1} \frac{L}{v_E} \propto E^{(d/2)-1} \quad (77)$$

Note that for $(k_E L)^{d-1}$ can be interpreted as the number of modes. Note also that for $d = 2$ the DOS is independent of energy and reflects the mass of the particle.

===== [2.7] Classical particle in magnetic field

For a particle in an arbitrary scalar potential $V(r)$ in 3D we get

$$Z(\beta) = \int \frac{dr dp}{(2\pi)^3} e^{-\beta \mathcal{H}} = \left(\frac{1}{\lambda_T} \right)^3 \int dr e^{-\beta V(r)} \quad (78)$$

Let us include also a vector potential:

$$\mathcal{H} = \frac{1}{2m} (p - eA(x))^2 + V(r) \quad (79)$$

$$Z = \int \frac{dr dp}{(2\pi)^3} e^{-\beta \left[\frac{1}{2m} (p - eA(x))^2 + V(x) \right]} = \int \frac{dr dp'}{(2\pi)^2} e^{-\beta \left[\frac{1}{2m} (p')^2 + V(x) \right]} \quad (80)$$

The result does not depend on $A(x)$. The energy spectrum is not affected from the existence of $A(x)$. The energies are $E = (1/2)mv^2 + V(x)$ irrespective of $A(x)$. To explain that the implicit assumption is having relaxation processes that makes the dynamics irrelevant. The classical diamagnetic effect disappears in the presence of relaxation. To discuss the effect of quantization.

===== [2.8] Gas of classical particles in a box

Let us consider N particles:

$$\mathcal{H} = \sum_{\alpha=1}^N \left[\frac{\vec{p}_{\alpha}^2}{2m} + V(r_{\alpha}) \right] + U(r_1, \dots, r_N) \quad (81)$$

In the absence of interaction the partition function is

$$Z_N(\beta) = \left(Z_1(\beta) \right)^N = \left[\frac{1}{\lambda_T^3} \int d^3x e^{-\beta V(x)} \right]^N \quad (82)$$

From now on we assume gas of identical particles and therefore include the Gibbs factor:

$$Z_N(\beta) \mapsto \frac{1}{N!} Z_N(\beta) \quad (83)$$

For N interacting particles we get

$$Z_N(\beta) = \frac{1}{N!} \left(\frac{1}{\lambda_T^3} \right)^N \int dr_1 \dots dr_N e^{-\beta U(r_1, \dots, r_N)} \quad (84)$$

===== [2.9] Two quantum identical particles

Let us see what is the partition function for a system that consists of two identical particles, say in a box. The total energy is written as $E_{ab} = E_a + E_b$. The partition function is

$$Z(\beta) = \frac{1}{2} \sum_{a \neq b} e^{-\beta(E_a + E_b)} + \left\{ \begin{matrix} 1 \\ 0 \end{matrix} \right\} \sum_a e^{-\beta(2E_a)} \quad (85)$$

$$= \frac{1}{2} \left(\sum_{a,b} e^{-\beta(E_a + E_b)} \pm \sum_a e^{-2\beta E_a} \right) = \frac{1}{2} \left[Z_1(\beta)^2 \pm Z_1(2\beta) \right] \quad (86)$$

For a particle in a d dimensional box

$$Z_1 = \left(\frac{L}{\lambda_T} \right)^d \quad (87)$$

$$Z_2 = \frac{1}{2} \left(Z_1^2 \pm 2^{-d/2} Z_1 \right) \quad (88)$$

Note that for $d = 3$ we get

$$Z_2(\beta) = \frac{1}{2} Z_1^2 \times \left[1 \pm \frac{1}{2^{3/2}} \left(\frac{\lambda_T^3}{\text{volume}} \right) \right] \quad (89)$$

The Fermi case is similar to hard sphere:

$$Z_2(\beta) = \frac{1}{2} Z_1^2 \times \left[1 - \left(\frac{\text{sphere volume}}{\text{box volume}} \right) \right] \quad (90)$$

===== [2.10] Two quantum particles in a box with interaction

The calculation of the partition function Z_2 for two identical quantum particle in a box, is both interesting and later on useful for the purpose of calculating the second virial coefficient of an N particle gas. The Hamiltonian is:

$$\mathcal{H} = \frac{P^2}{4m} + \frac{p^2}{m} + V(r) \quad (91)$$

In order to be able to do the calculation using separation of variables we cheat with the boundary conditions as follows: The center of mass motion is confined to a box of volume $V = (4\pi/3)R^3$, and the relative motion is confined by $|r| < R$ independently. Accordingly the partition function is factorizes as follows:

$$Z_2 = \left(2^{3/2} \frac{V}{\lambda_T^3} \right) \left[\sum'_{n\ell m} e^{-\beta E_{n\ell m}} \right] = \left(2^{3/2} \frac{V}{\lambda_T^3} \right) \left[\sum_b e^{-\beta E_b} + \int_0^\infty g(k) dk e^{-(\beta/m)k^2} \right] \quad (92)$$

where (n, ℓ, m) are the good quantum numbers for the relative motion. Ignoring the possibility of spin, the sum is over *even* or *odd* values of ℓ , for Bosons or Fermions respectively. In the second equality we separate the bound states from the scattering (continuum) states. In order to determine the DOS of the latter we recall that the radial wave functions are phase shifted spherical Bessel functions. Accordingly the box quantization condition for the allowed k_n values is

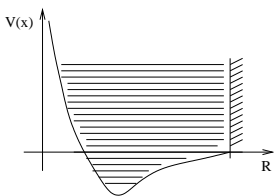
$$kR - \frac{\pi}{2}\ell + \delta_\ell = n\pi \quad (93)$$

From here one deduce a formula for the effect of the phase shifts on the DOS:

$$g(k) - g^{(0)}(k) = \frac{1}{\pi} \sum_\ell (2\ell + 1) \frac{\partial \delta_\ell}{\partial k} \quad (94)$$

Using this result we get after integration by parts the following expression for the interaction effect on the partition function:

$$Z_2 - Z_2^{(0)} = \left(2^{3/2} \frac{V}{\lambda_T^3} \right) \left[\sum_b e^{-\beta E_b} + \frac{\lambda_T^2}{\pi^2} \sum_\ell' \int_0^\infty k dk \delta_\ell(k) e^{-(\beta/m)k^2} \right] \quad (95)$$



[3] The canonical formalism

===== [3.1] The energy equation of state

Consider some system, for example particles that are confined in a box. The Hamiltonian is

$$\mathcal{H} = \mathcal{H}(\mathbf{r}, \mathbf{p}; X) \quad (96)$$

where X is some control parameter, for example the length of the box. Assuming that we are dealing with a *stationary* state, the energy of the system is

$$E \equiv \langle \mathcal{H} \rangle = \text{trace}(\mathcal{H}\rho) = \sum_r p_r E_r \quad (97)$$

If the system is prepared in a canonical states, then it is a mixture of energy eigenstates with probabilities

$$p_r = \frac{1}{Z} e^{-\beta E_r} \quad (98)$$

where the partition function is

$$Z(\beta, X) = \sum_r e^{-\beta E_r} \quad (99)$$

One observes that the energy of a system that is prepared in a canonical state can be derived from the partition function as follows:

$$E = \langle \mathcal{H} \rangle = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z = -\frac{\partial \ln Z}{\partial \beta} \quad (100)$$

Also one can find expressions for the higher moments, for example

$$\langle \mathcal{H}^2 \rangle = \frac{1}{Z} \frac{\partial}{\partial \beta} \frac{\partial}{\partial \beta} Z \quad (101)$$

In particular one deduces the relation

$$\text{Var}(E) = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial}{\partial \beta} Z \right) = T^2 \frac{\partial E}{\partial T} = T^2 C \quad (102)$$

where in the latter equality we have defined the temperature as $T = 1/\beta$ and the heat capacity as $C = dE/dT$. The notion of temperature will be discussed further below.

===== [3.2] The Equipartition theorem

In the classical context the Hamiltonian might be a sum of quadratic terms

$$\mathcal{H} = \sum_j c_j q_j^2 \quad (103)$$

where q_j are either coordinates of conjugate momenta. The partition function factorizes, where each quadratic term contributes a $\propto T^{1/2}$ term. It follows that each quadratic term contributes $T/2$ to the energy, and hence $1/2$ to the heat capacity.

This observation can be applied to the analysis of "balls connected by springs". We can always go to normal coordinates. The center of mass degree of freedom contributes $T/2$ to the energy, while each vibrational mode contributes T .

A formal extension of this so-called "Equipartition Theorem" is as follows:

$$\left\langle q_i \frac{\partial \mathcal{H}}{\partial q_j} \right\rangle = T \delta_{ij} \quad (104)$$

The proof is as follows: The measure of integration over phase space can be written as $dq_i dq_j dq'$, where q' represents all the other coordinates. Applying integration by parts we have

$$\int dq_i dq_j dq' q_i \frac{\partial \mathcal{H}(q)}{\partial q_j} e^{-\beta \mathcal{H}(q)} = -\frac{1}{\beta} \int dq_i dq_j dq' q_i \frac{\partial}{\partial q_j} \left[e^{-\beta \mathcal{H}(q)} \right] = \delta_{ij} \frac{1}{\beta} \int dq_i dq_j dq' e^{-\beta \mathcal{H}(q)} \quad (105)$$

and from here follows the Equipartition Theorem. This generalized version is useful in discussing particles that have interaction $u(x_i - x_j) \propto |x_i - x_j|^\alpha$, which constitutes a generalization of the harmonic ($\alpha = 2$) case.

===== [3.3] Heat capacity

From the Equipartition Theorem one deduce that the heat capacity of an "ideal" system equals to the effective number of freedoms: Each independent quadratic term in the Hamiltonian contributes $1/2$ to the heat capacity. This simple prescription should be refined for two reasons: (i) Degrees of freedom can "freeze" in the quantum treatment; (ii) In general a many body system is not ideal due to interactions. We first discuss the quantum issue referring to spins and oscillators.

Spin and oscillator.— For spin (+) or oscillator (-) with level spacing ω we have

$$\ln(Z(\beta)) = \pm \ln(1 \pm e^{-\beta\omega}) \quad (106)$$

$$E = -\frac{\partial \ln Z}{\partial \beta} = \frac{\omega}{e^{\beta\omega} \pm 1} \quad (107)$$

$$C(T) = \frac{dE}{dT} = \frac{e^{\omega/T}}{(e^{\omega/T} \pm 1)^2} \left(\frac{\omega}{T} \right)^2 \quad (108)$$

In both case the low temperature behavior of C is identical, namely, for $T \ll \omega$ it is dominated by the Boltzmann factor $e^{-\beta\omega}$. At high temperature C of the spin drop down because energy reaches saturation, while C of the oscillator approached unity reflecting the classical prediction $E \approx T$. Since $E = \omega n$ it is more illuminating to re-write the above results as follows:

$$\langle n \rangle = \frac{1}{e^{\beta\omega} \pm 1} \equiv f(\omega) \quad (109)$$

$$\text{Var}(n) = [1 \pm f(\omega)] f(\omega) \quad (110)$$

where $f(\omega)$ is known as the occupation function. In the case of an oscillator the result for the number variance can be regarded as a sum of a shot-noise particle-like term $\text{Var}(n) = \langle n \rangle$, and a classical term $\text{Var}(n) = \langle n \rangle^2$. In the case of a spin the fluctuations go to zero in both the "empty" and "full" occupation limits. It is customary in quantum-optics to characterize the fluctuations by $g^{(2)} = (\langle n^2 \rangle - \langle n \rangle^2) / \langle n \rangle^2$ and to say that the thermal result $g^{(2)} = 2$ corresponds to bouncing, while the "spin" result $g^{(2)} = 0$ corresponds to anti-bouncing. The value $g^{(2)} = 1$ reflects Poisson statistics and would apply in the case of coherent state preparation.

Debye model.— Let us refer further to a system that can be described as consisting of many harmonic freedoms, e.g. modes of vibrations. The spectral density of the modes might be $\propto \omega^{\alpha-1}$. For example in Debye model $\alpha = d = 3$, with some cutoff frequency ω_c . Then we get for the heat capacity

$$C(T) = \text{const} \int_0^{\omega_c} \frac{e^{\omega/T}}{(e^{\omega/T} - 1)^2} \left(\frac{\omega}{T}\right)^2 \omega^{\alpha-1} d\omega = \text{const} T^\alpha F\left(\frac{\omega_c}{T}\right) \quad (111)$$

where

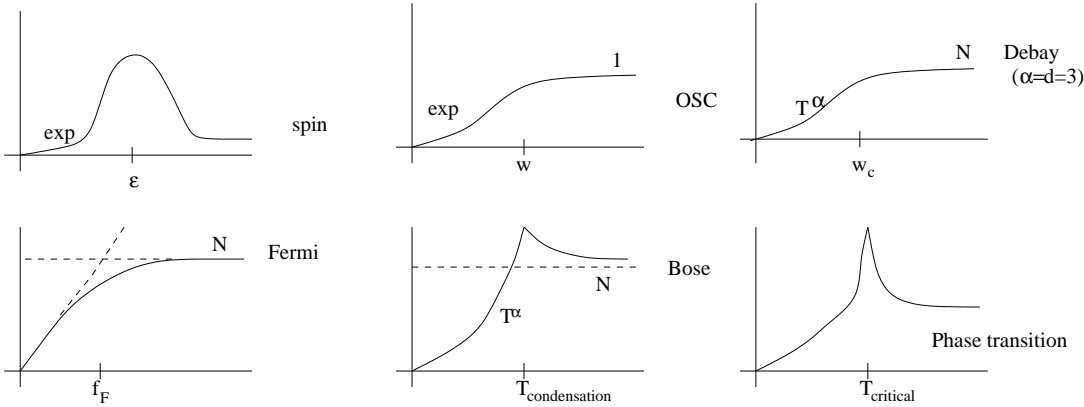
$$F(\nu) \equiv \int_0^\nu \frac{e^x}{(e^x - 1)^2} x^{1+\alpha} dx \quad (112)$$

The quantum result can be described as emerging from "freezing" of freedoms due to the quantization of energy. This phenomena has lead to the birth of quantum mechanics in the context of Black body radiation (Planck law).

Phase transitions.— We shall discuss phase transitions in later lectures. As the temperature is lowered towards a critical temperature T_c the system becomes "correlated", which means that the effective number of freedoms is reduced. We assume $T > T_c$ and note that similar picture applies if one approaches T_c from below. We can easily explain why the heat capacity diverges as T_c is approached. For an ideal gas the partition function is $Z = g^N$ where N is the number of independent particles, and $g = (L/\lambda_T)^d \propto T^{d/2}$ is the number of accessible states for a single particle that has a temperature T . For a correlated system $Z = g^{N_{\text{eff}}}$, where $N_{\text{eff}} = N/\xi^d$ is the effective number of independent regions, and ξ is called the correlation length. The prototype Ising model consist of spins ($g = 2$) and $\xi \propto |T - T_c|^{-\nu}$ where $\nu \approx 1/2$. Either we can write the expression for the heat capacity as follows:

$$C(T) = \frac{d \ln Z}{d(\ln T)} + \frac{d^2 \ln Z}{d(\ln T)^2} \equiv C_g(T) + C_\xi(T) \quad (113)$$

The non-singular term $C_g(T)$, that for an ideal gas equals $Nd/2$, originates from the dependence of g on the temperature, and is proportional to the effective number of freedoms. The singular term $C_\xi(T)$, that for Ising system is proportional to $|T - T_c|^{\nu d - 2}$, originates from the dependence of ξ on the temperature.



===== [3.4] The Virial theorem

Somewhat related to the equipartition theorem, is the Virial theorem. It is used to relate the expectation value of the “kinetic” and “potential” terms in Hamiltonian of the type $\mathcal{H} = K(p) + U(r)$.

Consider any observable G . It is clear that if the system is prepared in a *stationary* (not necessarily canonical) state, then the expectation value $\langle G \rangle$ is constant in time. By the rate of change equation of motion it follows that

$$\langle [\mathcal{H}, G] \rangle = 0 \quad (114)$$

In particular let us consider the generator of dilations

$$G = \frac{1}{2} \sum_j (r_j \cdot p_j + p_j \cdot r_j) \quad (115)$$

We get

$$\left\langle p \cdot \frac{\partial K}{\partial p} \right\rangle - \left\langle r \cdot \frac{\partial U}{\partial r} \right\rangle = 0 \quad (116)$$

with implicit summation over j . For quadratic $K(p)$ and $U(r)$ the first term equals $2\langle K \rangle$, and the second equals $-2\langle U \rangle$, and both equal $T/2$ if the classical equipartition theorem applies. More generally, for two-body interaction term of the type

$$U(r) = \sum_{\langle ij \rangle} u(r_i - r_j) = \sum_{\langle ij \rangle} |r_i - r_j|^\alpha \quad (117)$$

the second term in the Virial theorem equals $-\alpha\langle U \rangle$. This is a meaningful statement for $\alpha > 0$, otherwise there should be a “box” that confines the particles. See later discussion of how the “pressure” gets into the Virial theorem.

===== [3.5] Generalized forces

Assume that X is a parameter that appears in the Hamiltonian. We define the generalized force \mathcal{F} which is associated with the parameter X as

$$\mathcal{F} = -\frac{\partial \mathcal{H}}{\partial X} \quad (118)$$

This definition will be motivated later on when we discuss the notion of *work*. Here are some examples for generalized forces:

parameter	generalized force
piston displacement in cylinder with gas	Newtonian force
volume of a box with gas	Newtonian pressure
length of a polymer	Newtonian force (tension)
homogeneous electric field	total polarization
homogeneous magnetic field	total magnetization
magnetic flux through a ring	electric current

The last item deserves some more explanation. First we note that the current in a ring (times the area) is like magnetization. The direct identification of $\langle \mathcal{F} \rangle$ as the current is based on the following argumentation: If we make a change dX of the flux during a time dt , then the electro motive force (EMF) is $-dX/dt$, leading to a current \mathcal{I} in the ring. The energy increase of the ring is the EMF times the charge, namely $dE = (-dX/dt) \times (\mathcal{I}dt) = -\mathcal{I}dX$.

Given X and assuming that the system is prepared in a canonical state characterized by some β , we can derive the average value y of the generalized force \mathcal{F} from the partition function as follows:

$$y(X) \equiv \langle \mathcal{F} \rangle_X = \sum_r p_r \left(-\frac{E_r}{dX} \right) = \frac{1}{\beta} \frac{\partial \ln Z}{\partial X} \quad (119)$$

===== [3.6] Pressure on walls

Possibly the simplest point of view about pressure is to regard it as arising from collisions of particles with the walls. This is the so called the *kinetic picture* point of view. However, within the framework of the *canonical formalism* the pressure is defined as the generalized force that is associated with the volume, such that $dW = PdV$. It is quite puzzling that in the formal classical calculation the kinetic part factors out and the mass of the particles does not appear in the result:

$$\ln(Z(\beta, V)) = -\frac{3N}{2} \ln \beta + N \ln V + \text{const} \quad (120)$$

$$E = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2} NT \quad (121)$$

$$P = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{NT}{V} \quad (122)$$

With interactions we have to calculate a complicated configuration ($dr_1 dr_2 \dots dr_N$) integral. This calculation will be discussed in later sections. In the absence of interactions we see that the pressure is related to the kinetic energy, namely $P = (2/3)E/V$. Below we generalize this relation using the Virial theorem: we shall see that quite generally, both classically and quantum mechanically, the pressure is related to the kinetic and potential energy of the gas.

The volume deformation of a box is represented by a deformation field $D(r)$. To be specific let us write the Hamiltonian of N gas particles in a box as follows:

$$\mathcal{H} = K(p) + U(r) + V_L(r - \lambda D(r)) \quad (123)$$

Here $K(p)$ is the kinetic term, and $U(r)$ are the interactions, and $V_L(r)$ is box defining potential, and $\lambda = V - V_0$ is the deformation parameter. We want λ to equal the extra volume due to the deformation, and therefore normalize the displacement field such that

$$\oint D \cdot ds = 1, \quad \text{standard choice: } D(r) = \frac{1}{3V} r \quad (124)$$

Accordingly the definition and the expression for the pressure are

$$P = \left\langle -\frac{\partial \mathcal{H}}{\partial V} \right\rangle = \frac{1}{3V} \left\langle r \cdot \frac{\partial V_L}{\partial r} \right\rangle = \frac{1}{3V} \left[\left\langle p \cdot \frac{\partial K}{\partial p} \right\rangle - \left\langle r \cdot \frac{\partial U}{\partial r} \right\rangle \right] \quad (125)$$

where in the last equality we have used the Virial theorem. Note that this extends the discussion of the Virial theorem in previous section. The case of inter-atomic interactions with $\alpha > 0$ (bonded system with no walls) can be regarded formally as a special case of the above relation with $P = 0$. If $\alpha < 0$ there is non-zero pressure. We can use the equipartition theorem to get in the classical case

$$P = \frac{1}{V} \left[NT - \frac{1}{3} \left\langle r \cdot \frac{\partial U}{\partial r} \right\rangle \right] \quad (126)$$

where the first term is the same as in the law of ideal gases, while the second is due to the interactions, and can be expressed using moments of the inter-particle separation.

===== [3.7] Tension of polymer

The calculation of a tension of a polymer is very similar to the calculation of pressure. The parameter in the Hamiltonian is the length L of the polymer, which is analogous to the length or the volume of the box that contains the gas particles. In both cases the formal result depends only on the configuration integral, while the kinetic term factors out. Thus in both cases the result does not depend on the mass of the gas particles or on the mass of the monomers from which the polymer is composed. The partition function in the case of a polymer is

$$Z(\beta, L) = [\text{kinetic term}] \times \sum_{\text{conf.}} \delta(L - (x_1 + x_2 + \dots + x_N)) e^{-\beta U(\text{configuration})} \quad (127)$$

Typically, in analogy with the case of hard spheres, the potential energy merely restricts the space of allowed configurations. We see that up to a factor $Z(\beta, L)$ is the probability to observe length L . According to the central limit theorem for long polymer $Z(\beta, L) \propto \exp(-(1/2)(L/L_0)^2)$, where L_0 is the RMS average length of the polymer. Accordingly we get for the tension $F = (T/L_0^2)L$ as for a spring.

Optionally, if we insist on calculating directly the partition sum, it is simpler to imagine that a given tension F is applied on the polymer. The associated partition function is

$$Z_G(\beta, F) = [\text{kinetic term}] \times \sum_{\text{conf.}} e^{-\beta[U(\text{configuration}) - F \cdot (x_1 + x_2 + \dots + x_N)]} \quad (128)$$

If the potential energy of the polymer can be written as a sum $u(x_1) + u(x_2) + u(x_N)$ of independent terms, then $Z_G(\beta, F)$ can be factorized, reflecting that the total length of the polymer for a given tension is the sum of lengths of the monomers for the same tension. If required we can come back to $Z(\beta, L)$ by an inverse transform. Note that from mathematical point of view $Z(L)$ and $Z_G(F)$ are the probability function and its associated moment generating function, and we simply reconstruct here the procedure which is used to derive the central limit theorem.

===== [3.8] Polarization

The polarization is the generalized force that is associated with electric field. Let us assume that we have a bonded system of particles with an added uniform electric field:

$$\mathcal{H} = \sum_{\alpha} \frac{p_{\alpha}^2}{2m_{\alpha}} + \text{interactions} + \text{potential} - \sum_{\alpha} q_{\alpha} \mathcal{E} x_{\alpha} \quad (129)$$

$$\hat{P} = -\frac{\partial \mathcal{H}}{\partial \mathcal{E}} = \sum_{\alpha} q_{\alpha} \hat{x}_{\alpha} \quad (130)$$

The polarization \tilde{P} is the expectation value of \hat{P} .

===== [3.9] Magnetization

The magnetization is the generalized force that is associated with magnetic field. It is either due to having spin degree of freedom (Pauli) or due to the orbital motion. Here we clarify the definition using the three simplest examples.

Pauli magnetism.— Consider a collection of N spins. We denote the magnetic field by h . The Hamiltonian is

$$\mathcal{H} = -\sum_{\alpha=1}^N g_{\alpha} h S_z^{\alpha} \quad (131)$$

$$\hat{M} = -\frac{\partial \mathcal{H}}{\partial h} = \sum_{\alpha=1}^N g_{\alpha} S_z^{\alpha} \quad (132)$$

The magnetization \tilde{M} is the expectation value of \hat{M} .

Orbital magnetism (1D).— Consider a spinless particle in a ring of length L , and area A . The magnetic flux is $\Phi = hA$. The Hamiltonian is

$$\mathcal{H} = \frac{1}{2m} \left(p - e \frac{\Phi}{L} \right)^2 + V(x) \quad (133)$$

$$\hat{v} = i[\mathcal{H}, x] = \frac{1}{m} \left(p - e \frac{\Phi}{L} \right) \quad (134)$$

$$\hat{I} = -\frac{\partial \mathcal{H}}{\partial \Phi} = \frac{e}{L} \hat{v} \quad (135)$$

$$\hat{M} = -\frac{\partial \mathcal{H}}{\partial h} = A \hat{I} \quad (136)$$

The magnetization \tilde{M} is the expectation value of \hat{M} , or optionally we can refer to the circulating current I , which is the expectation value of \hat{I} .

Orbital magnetism (2D).— The more interesting case is the magnetization of electrons in a 2D box (3rd dimension does not play a role) due to the formation of Landau levels. We recall again that classically the energy spectrum of the system is not affected by magnetic field. But quantum mechanically Landau levels are formed (see "Lecture notes in Quantum mechanics"). Let us consider a box of area A that contains N spinless electrons. In the *bulk*, the energy of a Landau state that belongs to the ν level is $\varepsilon_\nu = (\nu + 1/2)\omega_B$ where $\omega_B = e\mathcal{B}/m$ is the cyclotron frequency. The degeneracy of each Landau level is $g_B = e\mathcal{B}A/2\pi$. The calculation of the single particle partition function is the same as that of harmonic oscillator (multiplied by the degeneracy). Assuming N electrons that can be treated as an ideal Boltzmann gas we get

$$\tilde{M} = -\frac{N}{12} \left(\frac{e}{m} \right)^2 \frac{\mathcal{B}}{T} + \mathcal{O}(\mathcal{B}^3) \quad (137)$$

This result does not hold for a low temperature electron gas, because the Fermi statistics of the occupation becomes important. Assuming zero temperature we define \mathcal{B}_n with $n = 1, 2, 3, \dots$ as the threshold value for which n Landau levels are fully filled. This values are determined by the equation $ng_B = N$. Considering first strong field $\mathcal{B} > \mathcal{B}_1$, the energy of the system is $E_0^{(N)} = N\omega_B/2$ and hence

$$\tilde{M} = -\frac{\partial E_0^{(N)}}{\partial \mathcal{B}} = -N \frac{e}{2m} \quad (138)$$

This result has a simple interpretation using "Bohr picture" of an orbiting electron: each electron performs a minimum energy cyclotron motion with unit angular momentum L , and associated magnetic moment $-(e/2m)L$. If the magnetic field is $\mathcal{B}_{n+1} < \mathcal{B} < \mathcal{B}_n$, one has to sum the energy of the electrons in n filled Landau levels, where the upper one is only partially filled. One obtain a quadratic expression from which it follows that the magnetization grows linearly from $-N(e/2m)$ to $+N(e/2m)$. Hence there is saw-tooth dependence of \tilde{M} on the field, which is known as the de Haas van Alphen (dHvA) oscillations.

There is a simple way to understand the dHvA result. For this purpose assume that A looks like a circle. Each "Landau state" occupies a strip that has a finite width. Within each strip there is a diamagnetic cyclotron motion whose net effect is like having an inner anticlockwise current ($I^\circ > 0$), and an outer clockwise current ($I^\circ < 0$). The total current of the strip is determined by the potential gradient (Hall effect): it is zero in the bulk, and positive along the edges. The bulk has diamagnetic contributions to the magnetization, because I° encloses a larger area compared with I° . When \mathcal{B} cross \mathcal{B}_n we get a jump in the magnetization that corresponds to the occupation of the edge states: The hall conductance of n Landau levels is $G_H = (e/2\pi)n$, residing in a region that experiences a potential difference ω_B . Hence the drop in the magnetization is $(G_H\omega_B) \times A = N(e/m)$.

===== [3.10] Empirical temperature

In practice we would like to be able to probe the β of the environment. For this purpose we use a thermometer. The simplest thermometer would be an ideal gas in a box, for which The partition function is

$$Z(\beta, V) = V^N \left(\frac{m}{2\pi\beta} \right)^{\frac{3N}{2}} \quad (139)$$

$$P = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{N}{V} \beta^{-1} \quad (140)$$

The empirical temperature is defined as follows:

$$\theta = \frac{PV}{N} = \frac{1}{\beta} \quad (141)$$

We can of course define different type of thermometers. The idea is simply to identify a measurable quantity that reflects the parameter β .

===== [3.11] Absolute temperature and entropy

If we *formally* vary X and β as parameters, then the canonical energy changes:

$$dE = \sum_r dp_r E_r + \sum_r p_r dE_r = \left[\left(\sum_r \frac{dp_r}{d\beta} E_r \right) d\beta + \left(\sum_r \frac{dp_r}{dX} E_r \right) dX \right] - y dX \quad (142)$$

The absolute temperature is *defined* as the integration factor of the first term

$$T = \text{integration factor} = \frac{1}{\beta} \quad (143)$$

such that

$$dE = T dS - y dX \quad (144)$$

The implied *definition* of the thermodynamic entropy is

$$S = - \sum p_r \ln p_r \quad (145)$$

Note that the thermodynamic entropy is an extensive quantity in the thermodynamic limit. It should not be confused with other types of "entropy". In particular we shall discuss the "Boltzmann entropy" in a later section with regard to the 2nd law of thermodynamics.

[4] Thermodynamics

===== [4.1] The Helmholtz function

At this stage it is convenient to define the Helmholtz generating function

$$F(T, X) \equiv -\frac{1}{\beta} \ln Z(\beta; X) \quad (146)$$

which allows to write the state equations in an elegant way:

$$S = -\frac{\partial F}{\partial T}, \quad y = -\frac{\partial F}{\partial X}, \quad E = F + TS \quad (147)$$

===== [4.2] Optional thermodynamic functions

State functions that describe physical systems can be derived from *generating functions*. The generating functions should be expressed using their canonical variables. Following formal mathematical procedures we can obtain from the Helmholtz function optional generating functions. The most popular are

$$F(T, X), \quad dF = -SdT - ydX \quad (148)$$

$$G(T, y) \equiv F + yX, \quad dG = -SdT + Xdy \quad (149)$$

$$E(S, X) \equiv F + TS, \quad dE = TdS - ydX \quad (150)$$

$$S(E, X), \quad dS = \frac{1}{T}dE + \frac{y}{T}dX \quad (151)$$

The derivatives of the state equations are known as the "thermodynamic constants" though they are not really constant...

$$C \equiv T \frac{\partial S}{\partial T} \quad (152)$$

$$\chi \equiv \frac{\partial y}{\partial X} \quad (153)$$

In the context of gases

$$\text{Compressibility} \equiv \frac{\partial V}{\partial P} \quad (154)$$

$$\text{ExpansionCoeff} \equiv \frac{\partial V}{\partial T} \quad (155)$$

===== [4.3] The Grand Hamiltonian approach

It is customary in thermodynamics to define "thermodynamic potentials" that are obtained from the Helmholtz free energy by means of Legendre transform. This can be regarded as a formal mathematical trick for switching the role of conjugate variables, but it also can be motivated physically. It is the same procedure that we had discussed regarding the calculation of the tension of a polymer. Here we repeat it with regard to a gas in a box with piston.

Let us regard the position of the piston (the parameter X) as a dynamical variable (let us call it x). We can apply force, say "electric" field \mathcal{E} on the piston. Accordingly the "grand Hamiltonian" of the system is

$$\mathcal{H}_G = \mathcal{H} + \mathcal{E}x + [\text{optional kinetic term}] \quad (156)$$

The optional kinetic term is required if the piston has finite mass, but its inclusion will not affect the analysis because it factors out of the calculation. The partition function is

$$Z_G(\beta, \mathcal{E}) = \sum_{x,r} e^{-\beta E_{x,r}} = \sum_x \exp \left[-\frac{F(T, x) + \mathcal{E}x}{T} \right] \quad (157)$$

$$\equiv \sum_x \exp \left[-\frac{G[x; T, \mathcal{E}]}{T} \right] \sim e^{-G(T, \mathcal{E})/T} \quad (158)$$

where $G(T, \mathcal{E}) = G[\bar{x}; T, \mathcal{E}]$, and the most probable value \bar{x} is obtained by minimizing $G[x; T, \mathcal{E}]$. This means that \bar{x} should be determined by solving the equation $\mathcal{E} = y(x)$. Accordingly we realize that $G(T, y)$ is the Legendre transform of $F(T, X)$. The roles of the conjugate variable X and y have been switched. If X and y are the volume V and the pressure P , then $G(T, P)$ is known as the Gibbs function.

===== [4.4] The chemical potential

Consider a gas that consists of N *identical* particles. This can be either *classical* or *quantum* gas (contrary to prevailing misconception, quantum mechanics is irrelevant to this issue - this will be explained in the "chemical equilibrium" lecture). Within the framework of the canonical formalism we define the chemical potential as follows:

$$\mu(T, V, N) \equiv \frac{\partial F}{\partial N} \quad (159)$$

Accordingly we have

$$dF = -SdT - PdV + \mu dN \quad (160)$$

$$dG = -SdT + VdP + \mu dN \quad (161)$$

The above definition of the chemical potential can be motivated by adopting a "grand Hamiltonian" perspective. Let us define a "grand system" that consists of the system and of a reservoir of particles. This reservoir consists of a huge collection of sites that hold a huge number of particles with binding energy μ . If we transfer N particle from the reservoir to the system the energy of the "grand system" becomes

$$\mathcal{H}_G = \mathcal{H} - \mu N \quad (162)$$

The so called grand partition function $Z_G(\beta, \mu)$ of the Grand system will be discussed in future lecture.

===== [4.5] The extensive property

At this stage it is appropriate to remark on a relation between the Gibbs function and the chemical potential that holds in the so-called thermodynamic limit. In this limit the system acquires an *extensive* property that can be formulated mathematically. Relating to the Gibbs function $G(T, P; N)$, one observes that if N is multiplied by some factor, then the volume V and the entropy S for the same (T, P) are expected to be multiplied by the same factor, and hence also G should be multiplied by the same factor. We therefore write

$$G(T, P, N) = N G(T, P, 1) \quad (163)$$

From $\mu = -dG/dN$ we deduce that the chemical potential is merely the Gibbs energy per particle. Consequently from the expression for dG it follows that

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP \quad (164)$$

===== [4.6] Work

In the definition of work the system and the environment are regarded as one driven *closed* unit. If we change X in time then from the “rate of change formula” we have the following exact expression:

$$\frac{dE}{dt} = \left\langle \frac{\partial \mathcal{H}}{\partial t} \right\rangle = -\langle \mathcal{F} \rangle_t \dot{X} \quad (165)$$

it follows that

$$\mathcal{W} \equiv \text{work done on the system} = E_{\text{final}} - E_{\text{initial}} = -\int \langle \mathcal{F} \rangle_t dX \quad (166)$$

This is an exact expression. Note that $\langle \mathcal{F} \rangle_t$ is calculated for the time dependent (evolving) state of the system. In a quasi-static adiabatic process one replaces $\langle \mathcal{F} \rangle_t$ by $\langle \mathcal{F} \rangle_{X(t)}$, where the notation $\langle \mathcal{F} \rangle_X$ implies that the system is assumed to be in a canonical state at any moment. More generally, within the frame work of linear response theory

$$\langle \mathcal{F} \rangle_t \approx \langle \mathcal{F} \rangle_X - \eta \dot{X} = y(X) - \eta \dot{X} \quad (167)$$

The first term is the conservative force, which is a function of X alone. The subscript implies that the expectation value is taken with respect to the instantaneous adiabatic state. The second term is the leading correction to the adiabatic approximation. It is the “friction” force which is proportional to the rate of the driving. The net conservative work is zero for a closed cycle while the “friction” leads to irreversible dissipation of energy with a rate

$$\dot{\mathcal{W}}_{\text{irreversible}} = \eta \dot{X}^2 \quad (168)$$

More generally it is customary to write

$$\mathcal{W} = -W + \mathcal{W}_{\text{irreversible}} \quad (169)$$

where the first term is the conservative work, or so to say “the work which is done by the system”

$$W = \int \langle \mathcal{F} \rangle_X dX = \int_{X_A}^{X_B} y(X) dX \quad (170)$$

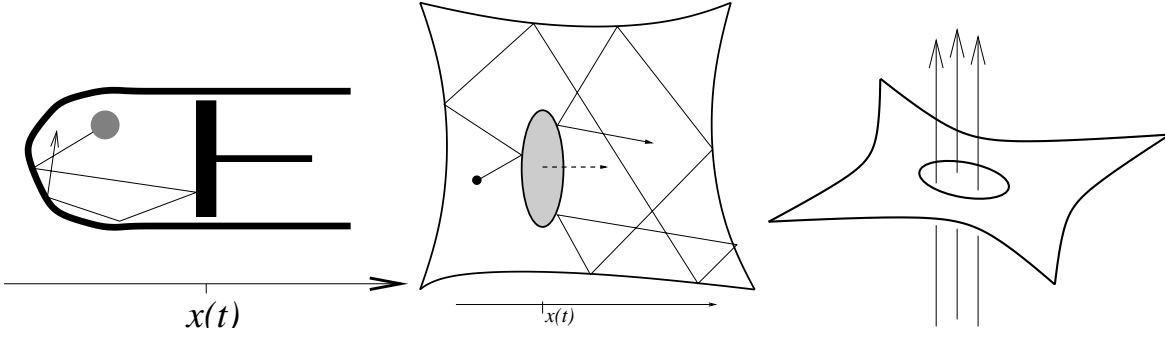
The two main examples that illustrate the above discussion are:

Example 1:

- X = position of a wall element (or scatterer)
- \dot{X} = wall (or scatterer) velocity
- $\langle \mathcal{F} \rangle$ = Newtonian force
- $-\eta \dot{X}$ = friction law
- $\eta \dot{X}^2$ = rate of heating

Example 2:

- X = magnetic flux through the ring
- $-\dot{X}$ = electro motive force
- $\langle \mathcal{F} \rangle$ = electrical current
- $-\eta \dot{X}$ = Ohm law
- $\eta \dot{X}^2$ = Joule law



==== [4.7] Heat

In order to understand which type of statements can be extracted from the canonical formalism we have to discuss carefully the physics of work and heat. We distinguish between the system and the environment and write the Hamiltonian in the form

$$\mathcal{H}_{\text{total}} = \mathcal{H}(\mathbf{r}, \mathbf{p}; X(t)) + \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{env}} \quad (171)$$

It is implicit that the interaction term is extremely small so it can be ignored in the calculation of the total energy. The environment is characterized by its temperature. More generally we assume that the environment consists of several “baths” that each has different temperature, and that the couplings to the baths can be switched on and off. Below we consider a *process* in which both the initial and the final states are equilibrated with a single bath. This requires that at the end of the driving process there is an extra waiting period that allows this equilibration. It is implied that both the initial and the final states of the system are canonical. Now we define

$$\mathcal{W} = \text{work} \equiv \left(\langle \mathcal{H}_{\text{total}} \rangle_B - \langle \mathcal{H}_{\text{total}} \rangle_A \right) \quad (172)$$

$$\mathcal{Q} = \text{heat} \equiv - \left(\langle \mathcal{H}_{\text{env}} \rangle_B - \langle \mathcal{H}_{\text{env}} \rangle_A \right) \quad (173)$$

$$E_{\text{final}} - E_{\text{initial}} \equiv \langle \mathcal{H} \rangle_B - \langle \mathcal{H} \rangle_A = \mathcal{Q} + \mathcal{W} \quad (174)$$

It is important to emphasize that the definition of work is the same as in the previous section, because we regard $\mathcal{H}_{\text{total}}$ as describing an isolated driven system. However, E is redefined as the energy of the system only, and therefore we have the additional term \mathcal{Q} in the last equation.

==== [4.8] Quasi static process

In general we have the formal identity:

$$dE = \sum_r dp_r E_r + \sum_r p_r dE_r \quad (175)$$

We would like to argue that in the adiabatic limit we can identify the first term as the heat dQ and the second term is the work $-dW$. One possible scenario is having no driving. Still we have control over the temperature of the environment. Assuming a quasi-static process we have

$$dX = 0 \quad (176)$$

$$dE = \sum_r dp_r E_r = T dS \quad (177)$$

$$dQ = T dS \quad (178)$$

$$dW = 0 \quad (179)$$

$$\mathcal{Q} = [E(B) - E(A)] \quad (180)$$

$$W = 0 \quad (181)$$

A second possible scenario is having an isolated systems going through an adiabatic process:

$$dp_r = 0 \quad (182)$$

$$dE = \sum_r p_r dE_r = -y dX \quad (183)$$

$$dQ = 0 \quad (184)$$

$$dW = y dX \quad (185)$$

$$Q = 0 \quad (186)$$

$$W = -[E(B) - E(A)] \quad (187)$$

Any general quasi-static process can be constructed from small steps as above, leading to

$$Q = \int_A^B T dS \quad (188)$$

$$W = \int_A^B y(X) dX \quad (189)$$

In particular for *isothermal* process we get

$$Q = T \times [S(B) - S(A)] \quad (190)$$

$$W = -[F(B) - F(A)] \quad (191)$$

If a process is both isothermal (constant T) and isobaric (constant P) we can still get work being done by changing some other parameter X , then we get

$$Q = T \times [S(B) - S(A)] \quad (192)$$

$$W = -[G(B) - G(A)] \quad (193)$$

===== [4.9] Cycles

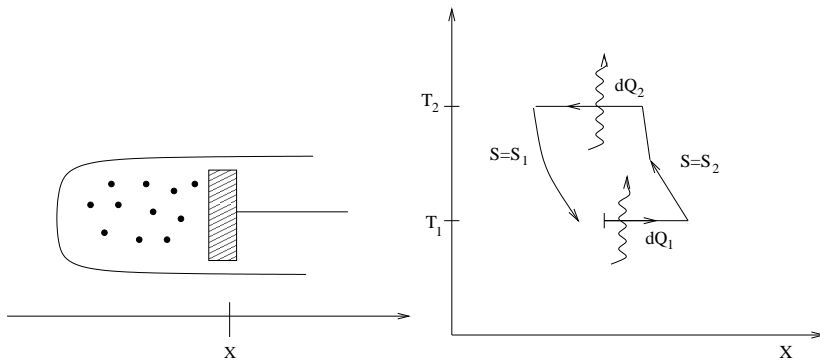
It is possible to design cycles in (X, T) space, such that the net effect is to convert heat into work (engine) or in reverse (heat pump). Consider for example a gas in a cylinder with a piston. If there is no restriction on the availability of baths the simplest engine could work as follows: Allow the gas to expand at high temperature; Lower the temperature; Compress the gas back by moving the piston back to its initial position; Raise back the temperature. The net effect here is to convert heat into work. The disadvantage of this cycle is that in order to make it reversible we need infinitely many intermediate baths in the heating and cooling stages. If we want to use a reversible cycle that uses two baths only we need the Carnot cycle. Then we can operate it also in reverse to get a heat pump.

Assuming that the levels become more dense as X is increased, it follows that the result of an adiabatic process would be a lower temperature (adiabatic cooling). If the process is isothermal rather than adiabatic there will be heat absorption (isothermal absorption) due to the re-distribution of the probabilities. These "rules of thumb" allow to gain intuition with regard to the operation of engines and heat-pumps.

The simplest system to consider is spin $S \gg 1$ in magnetic field. In order to be consistent with the piston example we define $X = -|h|$, so larger X is like larger volume, i.e. higher density of states. We consider a cycle that consists of 4 stages: adiabatic cooling to lower temperature; isothermal absorption stage ($Q_1 > 0$); adiabatic heating to higher temperature; and isothermal emission stage ($Q_2 < 0$). The net effect is to transfer heat from the cold bath to the hot bath, which requires to invest work.

At each stage the work W is positive or negative depending on whether the occupied levels go down or up respectively. The inclination is to say that during the adiabatic cooling stage the work is positive. This is true in the piston example, but not in general, as can be verified with the spin example. It should be clear that doing work on the system does not

imply that the its temperature becomes higher: the simplest demonstration would be to take an isolated container with gas to the top of Eiffel Tower: it requires work but the temperature is not affected. What is essential for the operation of the cycle is the variation in the *density* of the levels, irrespective of how they go up and down during the cycle.



[5] Chemical equilibrium and the Grand Canonical state

===== [5.1] The Gibbs prescription

In this lecture we are going to discuss chemical equilibrium. We shall see that the condition of chemical equilibrium involves the chemical potentials of the participating gases. For the purpose of calculating μ it is essential to find how the partition function depends on the number of particles. Classically the calculation of Z_N for a gas of *identical* particles is done using the Gibbs prescription:

$$Z_N[\text{Gibbs}] = \frac{1}{N!} Z_N[\text{distinguishable particles}] \quad (194)$$

We shall motivate this prescription in the following discussion of chemical equilibrium. For an ideal gas we get

$$Z_N = \frac{1}{N!} Z_1^N, \quad \text{where } Z_1 = \frac{V}{\lambda_T^3} \sum e^{-\beta \varepsilon_{\text{bound}}} \equiv g_0 \frac{V}{\lambda_T^3} \quad (195)$$

The summation is over the non-translational freedoms of the particle. Hence we get

$$\mu = -\frac{\partial F}{\partial N} = T \ln \left(\frac{N}{Z_1} \right) = \varepsilon_0 + T \ln \left(\frac{N}{V} \lambda_T^3 \right) \quad (196)$$

where in the last equality we have assumed that the particle has a single well defined binding energy. The inverse relation is

$$N = Z_1 e^{\beta \mu} = \frac{V}{\lambda_T^3} e^{-(\varepsilon_0 - \mu)/T} \quad (197)$$

The notion of identical particles:– The notion of *identical* particles does not require extra explanations if they are *indistinguishable* as in the quantum mechanical theory. Still we can ask what would happen if our world were classical. The answer is that in a classical reality one still has to maintain the Gibbs prescription if one wants to formulate a *convenient* theory for Chemical equilibrium. Namely, the condition for "chemical equilibrium" that we derive below has a simple form if we adopt the Gibbs prescription. Without the Gibbs prescription one would be forced to formulate an equivalent but non-friendly version for this condition.

===== [5.2] Chemical equilibrium

Consider the following prototype problem of chemical equilibrium:

$$A[a] \rightleftharpoons A[b] \quad (198)$$

where "a" and "b" are two phases, say to be in one of two regions in space, or to be either in the bulk or on the boundary of some bounded region. Given N identical particles we characterize the macroscopic occupation of the two phases by a reaction coordinate n , such that $N - n$ particles are in phase [a] and n particles are in phase [b]. The partition function is

$$Z_N^{ab} = \sum_n \left\{ \frac{N!}{(N-n)! n!} \right\} Z_{N-n}^a Z_n^b \quad (199)$$

The combinatorial "mixing" factor in the curly brackets counts the number of possibilities to divide N particles into two groups. It should be excluded if the particles are *indistinguishable*, as in the quantum theory. In the classical

theory, where the particles are *distinguishable* it should be included, but it can be absorbed into the definition of the partition function. This is what we call the “Gibbs prescription”. Using the Gibbs prescription the above sum can be re-written as follows:

$$Z_N^{ab} = \sum_n Z_{N-n}^a Z_n^b \quad (200)$$

The probability to have $(N-n, n)$ occupation is proportional to the n th term in the partition sum:

$$p(n) = \left\{ \frac{N!}{(N-n)!n!} \right\} \times \frac{Z_{N-n}^a Z_n^b}{Z_N^{ab}} = \frac{Z_{N-n}^a Z_n^b}{Z_N^{ab}} = C \exp [-\beta (F^a (N-n) + F^b (n))] \quad (201)$$

One should appreciate the usefulness of the Gibbs prescription. It is thanks to this prescription that the Free Energy is *additive*. If we did not use the Gibbs prescription we would be compelled to add in F a term that reflects “*mixing entropy*”. The most probable value \bar{n} is determined by looking for the largest term. This leads to the Chemical equilibrium condition:

$$F^a (N-n) + F^b (n) = \text{minimum} \quad (202)$$

$$\leadsto -\mu^a (N-n) + \mu^b (n) = 0 \quad (203)$$

Let us consider the case of ideal gases. Using the expression for μ we get

$$\frac{n}{N-n} = \frac{Z_1^b}{Z_1^a} \quad \leadsto \quad \bar{n} = N \frac{Z_1^b}{Z_1^a + Z_1^b} \quad (204)$$

This example is simple enough to allow a determination of the average value $\langle n \rangle$ too. The probability distribution of the reaction coordinate is

$$p(n) = \frac{N!}{(N-n)!n!} \frac{(Z_1^a)^{N-n} (Z_1^b)^n}{(Z_1^a + Z_1^b)^N} \quad (205)$$

leading to

$$\langle n \rangle = \sum_n p(n) n = \bar{n} \quad (206)$$

We see that the expectation value of n coincides with its typical (most probable) value. In the more general case of chemical equilibrium, as discussed below, this is an approximation that becomes valid for $N \gg 1$ in accordance with the central limit theorem.

===== [5.3] The law of mass action

This procedure is easily generalized. Consider for example

$$2C \rightleftharpoons 5A + 3B \quad (207)$$

Given that initially there are N_A particles of type A, N_B particles of type B, and N_C particles of type C we define a macroscopic reaction coordinate n such that $N_C - 2n$ is the number of particles of type C, and $N_A + 5n$ is the number of particles of type A, and $N_B + 3n$ is the number of particles of type B. Accordingly

$$Z^{abc} = \sum_n Z_{N_C-2n}^c Z_{N_A+5n}^a Z_{N_B+3n}^b \quad (208)$$

and

$$p(n) = \text{const } e^{-\beta(F^c(N_C-2n)+F^a(N_A+5n)+F^b(N_B+3n))} \quad (209)$$

leading to the equation

$$-2\mu^c(N_C-2n) + 5\mu^a(N_A+5n) + 3\mu^b(N_B+3n) = 0 \quad (210)$$

which with Boltzmann/Gibbs approximation becomes

$$\frac{(N_A+5n)^5(N_B+3n)^3}{(N_C-2n)^2} = \frac{(Z_1^a)^5(Z_1^b)^3}{(Z_1^c)^2} \quad (211)$$

or, assuming that [a],[b],[c] are all *volume* phases,

$$\frac{\left(\frac{N_A+5n}{V}\right)^5 \left(\frac{N_B+3n}{V}\right)^3}{\left(\frac{N_C-2n}{V}\right)^2} = \kappa(T) \quad (212)$$

where the reaction rate constant $\kappa(T) \propto e^{\varepsilon/T}$ depends on the reaction energy $\varepsilon = 2\varepsilon_c - 5\varepsilon_a - 3\varepsilon_b$.

===== [5.4] Equilibrium in pair creation reaction

Consider the reaction

$$\gamma + \gamma \rightleftharpoons e^+ + e^- \quad (213)$$

This can be analyzed like a chemical reaction $C \rightleftharpoons A + B$, which is of the same type as considered in the previous version. The important point to notice is that Z^c is independent of n , and therefore the chemical potential of the electromagnetic field is formally $\mu^c = 0$. The electromagnetic field is like a "bath", so if we regard it as part of the environment, so we could have written vacuum $\rightleftharpoons e^+ + e^-$. In any case we get at equilibrium

$$\mu^{e^+}(n_1) + \mu^{e^-}(n_2) = 0 \quad (214)$$

where in the Boltzmann/Gibbs approximation

$$\mu(n) \approx mc^2 + T \ln \left(\frac{n\lambda_T^3}{V} \right) \quad (215)$$

leading to

$$n_1 n_2 = \left(\frac{V}{\lambda_T^3} \right)^2 e^{-2mc^2/T} \quad (216)$$

This problem is formally the same as that of a semiconductor where e^+ and e^- are the holes and the electrons, and $2mc^2$ corresponds to the energy gap between the valance and the conduction bands.

===== [5.5] Equilibrium in liquid-gas system

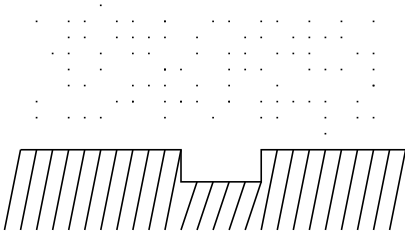
The equilibrium between a liquid phase and a gaseous phase is just another example for a chemical equilibrium. We can write the equation that determines the coexistence curve in (T, P) diagram as $[\mu_a(T, P) - \mu_b(T, P)] = 0$. By implicit differentiation of this equation with respect to T we get the Clausius-Clapeyron relation

$$\left. \frac{dP}{dT} \right|_{\text{coexistence}} = - \frac{\partial_T [\mu_a - \mu_b]}{\partial_P [\mu_a - \mu_b]} = \frac{\Delta S}{\Delta V} = \frac{1}{T} \frac{[\text{Latent heat}]}{[\text{Volume change}]} \quad (217)$$

Outside of the coexistence curve either μ_a or μ_b are smaller, and accordingly all the particles occupy one phase only.

===== [5.6] Site system

The chemical potential can be calculate easily for a system of N identical particles that occupy a set of M sites (or modes) that have the same binding energy ε . Since we assume that the biding energy is the same for all sites, it follows that estimating Z_1 is essentially a combinatorial problem. We assume $n \gg 1$ so we can approximate the derivative of $\ln(n!)$ as $\ln(n)$. We also write the result for the most probable n which is obtained given μ . Note that the result for \bar{n} is meaningful only for large M .



Fermionic site:— Each site can have at most one particle

$$Z_n = \frac{M!}{n!(M-n)!} e^{-\beta \varepsilon n} \quad (218)$$

$$\mu = \varepsilon + T \ln \left(\frac{n}{M-n} \right) \quad (219)$$

$$\bar{n} = M(e^{\beta(\varepsilon - \mu)} + 1)^{-1} \quad (220)$$

Bosonic site:— Each site can have any number of particles. The combinatorial problem is solved by asking how many ways to divide n particles in a row with $M-1$ partitions. If the particles were distinct the result would be $(n + (M-1))!$. Taking into account that the particles are indistinguishable we get

$$Z_n = \frac{(n + M - 1)!}{n!(M-1)!} e^{-\beta \varepsilon n} \quad (221)$$

$$\mu = \varepsilon + T \ln \left(\frac{n}{(M-1) + n} \right) \quad (222)$$

$$\bar{n} = (M-1)(e^{\beta(\varepsilon - \mu)} - 1)^{-1} \quad (223)$$

Electromagnetic mode:— Each mode of the electromagnetic field can be regarded as a Bosonic site that can occupy photons with binding energy ω . Since n is not constrained it follows formally that

$$\mu = 0 \quad (224)$$

$$\bar{n} = (e^{\beta \omega} - 1)^{-1} \quad (225)$$

Boltzmann approximation:— Assuming dilute occupation ($1 \ll n \ll M$) we get a common approximation for both Fermi and Bose case:

$$Z_n = \frac{M^n}{n!} e^{-\beta \varepsilon n} \quad (226)$$

$$\mu = \varepsilon + T \ln \left(\frac{n}{M} \right) \quad (227)$$

$$\bar{n} = M e^{-\beta(\varepsilon - \mu)} \quad (228)$$

General system of sites:— If we want to consider the partition function of N particles in M sites that have different binding energies we have to calculate

$$Z_N(\beta) = \sum_{n_1 + \dots + n_M = N} e^{-\beta(\varepsilon_1 n_1 + \dots + \varepsilon_M n_M)} \quad (229)$$

Because of the constraint the sum cannot be factorized. We therefore adopt the "Grand Hamiltonian" strategy and calculate the Grand partition function $\mathcal{Z}(\beta, \mu)$ that corresponds to $\mathcal{H}_G = \mathcal{H} - \mu N$. In principle we can get $Z_N(\beta)$ from $\mathcal{Z}(\beta, \mu)$ via an inverse transform, but in practice it is more convenient to stay with the Grand Hamiltonian framework.

===== [5.7] The grand canonical formalism

We can regard the grand canonical formalism as a special case of the canonical formalism, where the Grand Hamiltonian $\mathcal{H}_G = \mathcal{H} - \mu N$ describes a Grand system that consists of the gas particles and a hypothetical reservoir. Optionally we can motivate the introduction of the grand canonical formalism following the same justification strategy as in the case of the canonical formalism. First we have to specify the many body eigenstates R of the system:

$$\hat{N}|R\rangle = N_R|R\rangle \quad (230)$$

$$\hat{H}|R\rangle = E_R|R\rangle \quad (231)$$

Then we assume that the system can exchange particles as well as energy with the environment. The probability of a many body eigenstate R is

$$p_R = \frac{e^{-\beta E_R} Z_{N-N}^{\text{env}}}{Z_{\text{sys+env}}}, \quad \text{with } Z_{N-N}^{\text{env}} \propto e^{\beta \mu N} \quad (232)$$

We deduce that

$$p_R = \frac{1}{\mathcal{Z}} e^{-\beta(E_R - \mu N_R)} \quad (233)$$

where the normalization constant is

$$\mathcal{Z}(\beta, \mu) \equiv \sum_R e^{-\beta(E_R - \mu N_R)} \quad (234)$$

The Grand Canonical $\mathcal{Z}(\beta, \mu)$ is defined in complete analogy with the canonical case as sum over the many body states "R". For some purposes it is convenient to write it as a function $\mathcal{Z}(z; \beta)$ of the fugacity:

$$z \equiv e^{\beta \mu}, \quad \frac{1}{\beta} \frac{\partial}{\partial \mu} = z \frac{\partial}{\partial z} \quad (235)$$

The Grand Canonical $\mathcal{Z}(\beta, \mu)$ can serve as a generating function as follows:

$$N \equiv \langle \hat{N} \rangle = \sum_R p_R N_R = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} \quad (236)$$

$$E - \mu N = - \frac{\partial \ln \mathcal{Z}}{\partial \beta} \quad (237)$$

$$P \equiv \left\langle - \frac{\partial H}{\partial V} \right\rangle = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial V} \quad (238)$$

Equivalently

$$F_G(T, V, \mu) \equiv - \frac{1}{\beta} \ln \mathcal{Z} \quad (239)$$

$$N = - \frac{\partial F_G}{\partial \mu} \quad (240)$$

$$P = - \frac{\partial F_G}{\partial V} \quad (241)$$

$$S = - \frac{\partial F_G}{\partial T} \quad (242)$$

$$E = F_G + TS + \mu N \quad (243)$$

In the thermodynamic limit F_G is extensive, also in the case of non ideal gas. Consequently

$$F_G(T, V, \mu) = -VP(T, \mu) \quad (244)$$

$$dP = \frac{S}{V} dT + \frac{N}{V} d\mu \quad (245)$$

In other words rather than using the notation F_G , we can regard $P(T, \mu)$ as the generating function. Note that this is the "Grand canonical" version of the "canonical" Gibbs function relation

$$d\mu = - \frac{S}{N} dT + \frac{V}{N} dP \quad (246)$$

For constant T , a variation in the chemical potential is related to a variation $dP = nd\mu$ in the pressure, where $n = N/V$ is the density. It is common to define the compressibility of the gas as follows:

$$\kappa_T = \frac{1}{n} \frac{dn}{dP} = \frac{1}{n^2} \frac{dn}{d\mu} \quad (247)$$

===== [5.8] Fermi occupation

A site or mode can occupy $n = 0, 1$ particles. The binding energy is ϵ . the site is in thermochemical equilibrium with a gas in temperature β and chemical potential μ .

$$N_n = n \quad (248)$$

$$E_n = n\epsilon \quad (249)$$

$$p_n = \frac{1}{\mathcal{Z}} e^{-\beta(\epsilon - \mu)n} \quad (250)$$

and accordingly,

$$\mathcal{Z}(\beta, \mu) = \left(1 + e^{-\beta(\epsilon - \mu)}\right) \quad (251)$$

$$N(\beta, \mu) = \langle \hat{n} \rangle = \sum_n p_n n = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \equiv f(\epsilon - \mu) \quad (252)$$

$$E(\beta, \mu) = \langle \hat{n}\epsilon \rangle = \epsilon f(\epsilon - \mu) \quad (253)$$

We have defined the Fermi occupation function $0 \leq f(\epsilon - \mu) \leq 1$

===== [5.9] Bose occupation

A site or mode can occupy $n = 0, 1, 2, 3, \dots$ particles. The binding energy is ϵ . the site is in thermochemical equilibrium with a gas in temperature β and chemical potential μ .

$$N_n = n \quad (254)$$

$$E_n = n\epsilon \quad (255)$$

$$p_n = \frac{1}{\mathcal{Z}} e^{-\beta(\epsilon - \mu)n} \quad (256)$$

and accordingly,

$$\mathcal{Z}(\beta, \mu) = \left(1 - e^{-\beta(\epsilon - \mu)}\right)^{-1} \quad (257)$$

$$N(\beta, \mu) = \langle \hat{n} \rangle = \sum_n p_n n = \frac{1}{e^{\beta(\epsilon - \mu)} - 1} \equiv f(\epsilon - \mu) \quad (258)$$

$$E(\beta, \mu) = \langle \hat{n}\epsilon \rangle = \epsilon f(\epsilon - \mu) \quad (259)$$

We have defined the Bose occupation function $0 \leq f(\epsilon - \mu) \leq \infty$. If $\epsilon < \mu$ then $\langle n \rangle \rightarrow \infty$. If $\epsilon = \mu$ then the site may have any occupation. If $\epsilon > \mu$ then $\langle n \rangle$ is finite.

===== [5.10] Bosonic mode occupation

The occupation of a mode of vibration, say the number photons in an electromagnetic mode, or the number of phonons in a vibration mode, are described by the canonical ensemble, by can be optionally regarded as described by the grand-canonical ensemble with $\mu = 0$. With slight change in notations we have:

$$N_n = n \quad (260)$$

$$E_n = n\omega \quad (261)$$

$$p_n = \frac{1}{Z} e^{-\beta\omega n} \quad (262)$$

and accordingly,

$$Z(\beta) = \left(1 - e^{-\beta\omega}\right)^{-1} \quad (263)$$

$$N(\beta) = \langle \hat{n} \rangle = \sum_n p_n n = \frac{1}{e^{\beta\omega} - 1} \equiv f(\omega) \quad (264)$$

$$E(\beta) = \langle \hat{n}\omega \rangle = \omega f(\omega) \quad (265)$$

[6] Quantum ideal gases

===== [6.1] Equations of state

In what follows, unless written otherwise $\epsilon = 0$ is the ground state and

$$\sum_r \rightarrow \int_0^\infty g(\epsilon) d\epsilon \quad (266)$$

The stationary states of the multi particle system are occupation states

$$|\mathbf{n}\rangle = |n_1, n_2, n_3, \dots, n_r, \dots\rangle \quad (267)$$

where $n_r = 0, 1$ for Fermi occupation and $n_r = 0, 1, 2, 3, 4, \dots$ for Bose occupation. For these states we have

$$N_{\mathbf{n}} = \sum_r n_r \quad (268)$$

$$E_{\mathbf{n}} = \sum_r n_r E_r \quad (269)$$

$$p_{\mathbf{n}} \propto e^{-\beta \sum_r (\epsilon_r - \mu) n_r} \quad (270)$$

which can be factorized. This means that each site or mode can be treated as an independent system. We use E and N without index for the expectation values in an equilibrium state. For the Fermionic and Bosonic case we have respectively (\pm)

$$\ln Z = \pm \sum_r \ln(1 \pm e^{-\beta(\epsilon_r - \mu)}) = \beta \int_0^\infty \mathcal{N}(\epsilon) d\epsilon f(\epsilon - \mu) \quad (271)$$

$$N = \sum_r \langle \hat{n}_r \rangle = \sum_r f(\epsilon_r - \mu) = \int_0^\infty g(\epsilon) d\epsilon f(\epsilon - \mu) \quad (272)$$

$$E = \sum_r \epsilon_r \langle \hat{n}_r \rangle = \sum_r f(\epsilon_r - \mu) \epsilon_r = \int_0^\infty g(\epsilon) \epsilon d\epsilon f(\epsilon - \mu) \quad (273)$$

$$P = \frac{1}{\beta} \frac{\ln Z}{V} = \frac{1}{V} \int_0^\infty \mathcal{N}(\epsilon) d\epsilon f(\epsilon - \mu) \quad (274)$$

It is good to remember that $P(T, \mu)$ can serve as a generating function for all other state equations. This would be true also if the gas were not ideal. In particular $N/V = dP/d\mu$ relates the density to the chemical potential, which implies a relation between the the pressure P and the density N/V .

===== [6.2] Explicit expressions for the state equations

We assume one particle states $|r\rangle$ that have the density

$$g(\epsilon) = V c \epsilon^{\alpha-1}, \quad \mathcal{N}(E) = \frac{1}{\alpha} \epsilon g(\epsilon) \quad (275)$$

For a particle in d dimensional box $\alpha = d/\nu$ where ν is the exponent of the dispersion relation $\epsilon \propto |p|^\nu$, and c is a constant which is related to the mass m . For example, in the case of spin 1/2 particle in 3D space we have

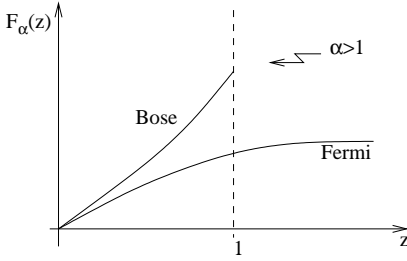
$$g(\epsilon) = 2 \times V \frac{(2m)^{3/2}}{(2\pi)^2} \epsilon^{\frac{1}{2}} \quad (276)$$

The following integral is useful:

$$F_\alpha(z) \equiv \int_0^\infty \left(\frac{1}{z} e^x \pm 1 \right)^{-1} x^{\alpha-1} dx \equiv \pm \Gamma(\alpha) \text{Li}_\alpha(\pm z) \quad (277)$$

where the \pm refer to Bose and Fermi case respectively. Details of the Polylogarithm function $\text{Li}_\alpha(z)$ can be found in Wikipedia. In the physics community it is commonly denoted as $g_\alpha(z)$. Note that

$$\text{Li}_\alpha(z) \equiv \sum_{\ell=1}^{\infty} \frac{1}{\ell^\alpha} z^\ell = z + \dots, \quad \text{Li}_\alpha(1) \equiv \zeta(\alpha) \quad (278)$$



For larger values of z the function $F_\alpha(z)$ grows faster in the case of a Bose occupation. In the latter case it either diverges or attains a finite value as $z \rightarrow 1$, namely $F_\alpha(1) = \Gamma(\alpha)\zeta(\alpha)$. The latter expression gives a finite result for $\alpha > 1$. In particular we have $\Gamma(3/2) = \sqrt{\pi}/2$ and $\zeta(3/2) \approx 2.612$. In the Fermi case the integral is always finite. Using the step-like behavior of the Fermi occupation function we get for $z \gg 1$

$$F_\alpha(z \gg 1) \approx \frac{1}{\alpha} (\ln z)^\alpha \quad (279)$$

We can express the state equations using this integral, where z is identified as the fugacity. We get

$$\frac{N}{V} = cT^\alpha F_\alpha(z) \quad (280)$$

$$\frac{E}{V} = cT^{\alpha+1} F_{\alpha+1}(z) \quad (281)$$

while P is related trivially to the energy:

$$P = \frac{1}{\beta} \left(\frac{\ln \mathcal{Z}}{V} \right) = \frac{1}{\alpha} \left(\frac{E}{V} \right) \quad (282)$$

The specific results in the case of a spin 0 non-relativistic Bose particles are:

$$\frac{N}{V} = \frac{1}{\lambda_T^3} \text{Li}_{3/2}(z) \quad (283)$$

$$\frac{E}{V} = \frac{3}{2} \frac{T}{\lambda_T^3} \text{Li}_{5/2}(z) \quad (284)$$

$$P = \frac{2}{3} \left(\frac{E}{V} \right) = \frac{T}{\lambda_T^3} \text{Li}_{5/2}(z) \quad (285)$$

For more details see Huang p.231-232;242.

[6.3] Ideal gases in the Boltzmann approximation

We take $\epsilon = 0$ as the ground state energy of the one-particle states. The Boltzmann approximation is

$$f(\epsilon - \mu) \approx e^{-\beta(\epsilon - \mu)} \quad (286)$$

It holds whenever the occupation is $f() \ll 1$. If it is valid for the ground state $\epsilon = 0$, then it is valid globally for all the higher levels. Accordingly the validity condition is:

$$z = e^{\beta\mu} \ll 1 \quad \Rightarrow \quad \text{Li}(z) \approx z \quad (287)$$

In the case of standard 3D gas the Boltzmann approximation condition can be rewritten as

$$N\lambda_T^3 \ll V \quad \rightsquigarrow \quad T \gg T_c \text{ (Bosons)}, \quad \rightsquigarrow \quad T \gg T_F \text{ (Fermions)} \quad (288)$$

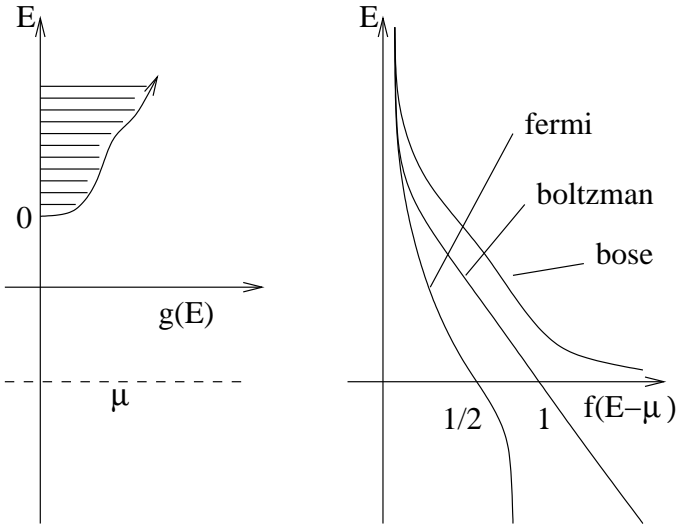
We shall defined the condensation temperature (T_c) and the Fermi energy (T_F) is later sections. Within the framework of the Boltzmann approximation we can re-derive the classical equation of an ideal gas:

$$\frac{N}{V} = \frac{1}{\lambda_T^3} z = \frac{1}{\lambda_T^3} e^{\mu/T} \quad (289)$$

$$\frac{E}{V} = \frac{3}{2} \frac{T}{\lambda_T^3} z = \frac{3}{2} \frac{N}{V} T \quad (290)$$

$$P = \frac{T}{\lambda_T^3} z = \frac{N}{V} T \quad (291)$$

Note that within this approximation E and P do not depend on the mass of the particles.



[6.4] Bose Einstein condensation

Let us write again the general expression for the occupation of the orbitals:

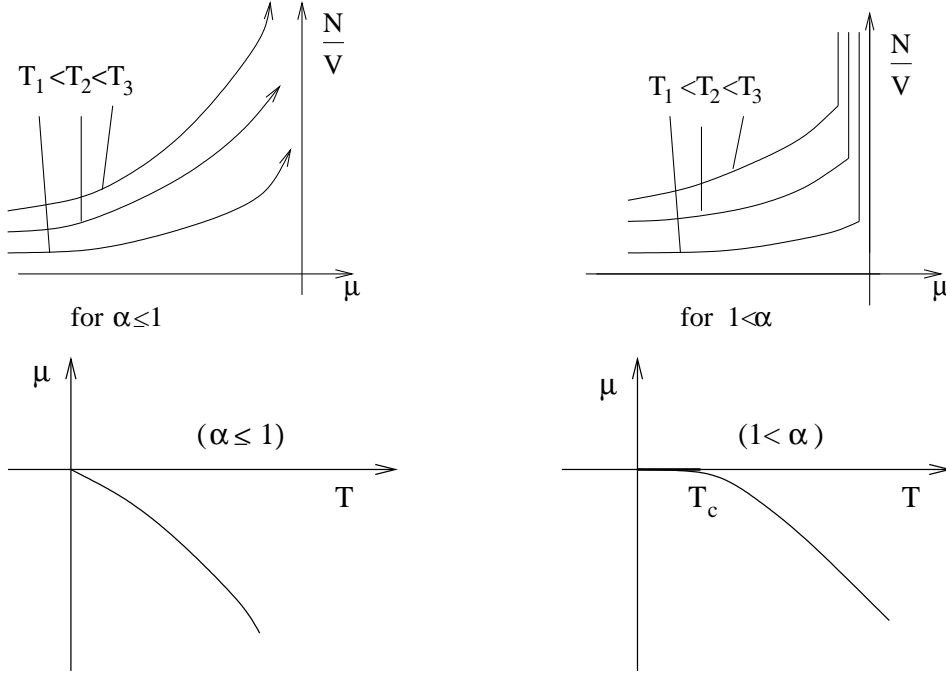
$$\frac{N}{V}(\beta, \mu) = c \int \epsilon^{\alpha-1} d\epsilon \left(\frac{1}{e^{\beta(\epsilon - \mu)} - 1} \right) \quad (292)$$

we get

$$\frac{N}{V}(\beta, \mu \rightarrow 0^-) = \infty \text{ for } \alpha \leq 1 \quad (293)$$

while for $\alpha > 1$ only a finite fraction can be accommodated:

$$\frac{N}{V}(\beta, \mu \rightarrow 0^-) = c\Gamma(\alpha)\zeta(\alpha)T^\alpha \text{ for } \alpha > 1 \quad (294)$$



In the latter case, of $\alpha > 1$, having $\mu = 0$ implies

$$\frac{N}{V}(\beta, \mu=0) = \frac{\langle n \rangle_0}{V} + c\Gamma(\alpha)\zeta(\alpha)T^\alpha \quad (295)$$

while

$$E = cV\Gamma(\alpha+1)\zeta(\alpha+1)T^{\alpha+1} \quad (296)$$

$$P = \frac{1}{\alpha} \left(\frac{E}{V} \right) \quad (297)$$

In particular the standard results for condensation in 3D are

$$N = n_0 + V\zeta\left(\frac{3}{2}\right)\left(\frac{m}{2\pi}\right)^{\frac{3}{2}}T^{\frac{3}{2}} \quad (298)$$

$$P = \zeta\left(\frac{5}{2}\right)\left(\frac{m}{2\pi}\right)^{\frac{5}{2}}T^{\frac{5}{2}} \quad (299)$$

The pressure P is independent of the total number of particles, because the condensate does not have any contribution. Hence the compressibility $\kappa \propto (\partial P / \partial V)^{-1} = \infty$. If we change the volume the extra/missing particles just come from the ground state, which is like a reservoir of $\mu = 0$ particles.

Given T , if we push N particles into a box, the condition to have condensation is $N > N(\beta, \mu \rightarrow 0^-)$. The condensation temperature, below which $\mu = 0$, is

$$T_c = \left(\frac{1}{c\Gamma(\alpha)\zeta(\alpha)} \frac{N}{V} \right)^{1/\alpha} \propto \frac{1}{m\ell^2} \quad (300)$$

where ℓ is the average distance between the particles. Given N , if one tries to eliminate μ , and writes it as a function of T , then one observes that below the condensation temperature μ is forced to become zero. Under such circumstances all the particles that cannot be occupied in the excited states have to condense in the ground state:

$$\frac{\langle n \rangle_0}{V} = \frac{N}{V} - \frac{N}{V} (\beta, \mu \rightarrow 0^-) = \left(1 - \left(\frac{T}{T_c}\right)^\alpha\right) \frac{N}{V} \quad (301)$$

The common phrasing is that a macroscopic fraction of the particles occupies the ground state. This fraction is determined by $(T/T_c)^\alpha$ or equivalently by V/λ_T . Note that $T \gg T_c$ is an optional way to write the Boltzmann condition.

===== [6.5] Fermi gas at low temperatures

At zero temperatures the Fermi function is a step function. At finite temperatures the step is smeared over a range T . In order to find explicit expressions for the state functions we have to perform an integral that involves the product of $f(\epsilon)$ with a smooth function $g(\epsilon)$. The latter is the density of states $\mathbf{g}(\epsilon)$ if we are interested in N , or $\epsilon \mathbf{g}(\epsilon)$ if we are interested in E . There is a simple procedure to get an approximation say to second order in T . For this purpose we first define the zero temperature result

$$G(\mu) \equiv \int_{-\infty}^{\mu} g(\epsilon) d\epsilon \quad (302)$$

And then proceed with the finite temperature calculation using integration by parts:

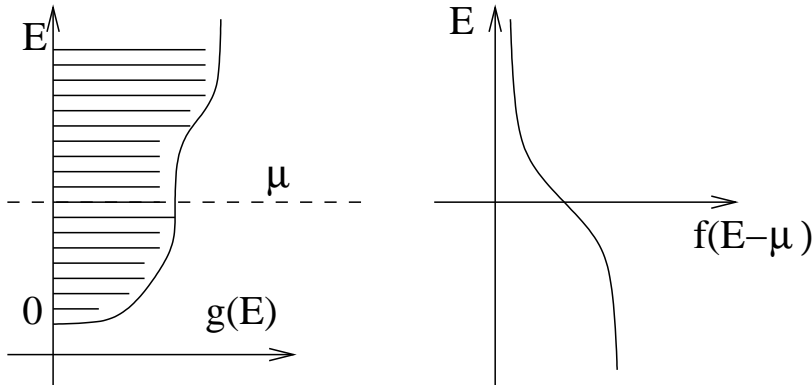
$$\int_{-\infty}^{\infty} d\epsilon g(\epsilon) f(\epsilon - \mu) = \int_{-\infty}^{\infty} d\epsilon G(\epsilon) [-f'(\epsilon - \mu)] \equiv \int_{-\infty}^{\infty} d\epsilon G(\epsilon) \delta_T(\epsilon - \mu) \quad (303)$$

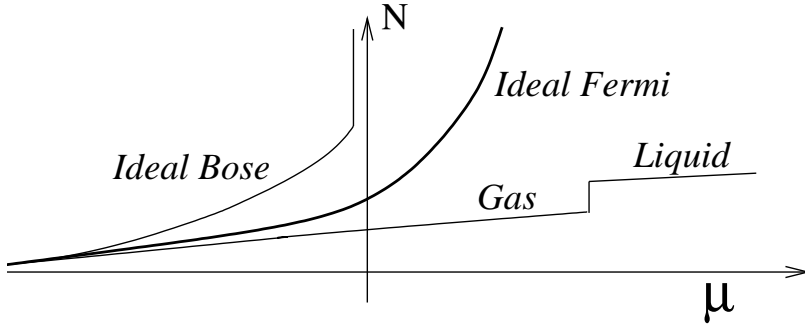
$$= \int_{-\infty}^{\infty} d\epsilon \left[G(\mu) + G'(\mu)(\epsilon - \mu) + \frac{1}{2} G''(\mu)(\epsilon - \mu)^2 + \dots \right] \delta_T(\epsilon - \mu) \quad (304)$$

$$= G(\mu) + \frac{\pi^2}{6} T^2 g'(\mu) + \mathcal{O}(T^4) \quad (305)$$

We can apply this formula to the $N = \mathcal{N}(\mu)$ calculation. First we do the zero temperature integral, and from it eliminate μ as a function of N . This zero temperature result is known as the Fermi energy $\mu = \epsilon_F$. Then we substitute $\mu = \epsilon_F + \delta\mu$ in the above second order expression, expand $G(\mu) \approx G(\epsilon_F) + \mathbf{g}(\epsilon_F) \delta\mu$, and find

$$\mu(T) \approx \epsilon_F - \frac{\pi^2}{6} \frac{\mathbf{g}'(\epsilon_F)}{\mathbf{g}(\epsilon_F)} T^2 + \mathcal{O}(T^4) \quad (306)$$





The specific result for N in the case of a power law DOS is:

$$N = \frac{1}{\alpha} c V \mu^\alpha \left(1 + \alpha (\alpha - 1) \frac{\pi^2}{6} \left(\frac{T}{\mu} \right)^2 + \dots \right) \quad (307)$$

leading after elimination to

$$\epsilon_F = \left(\frac{\alpha N}{c V} \right)^{\frac{1}{\alpha}} \quad (308)$$

$$\mu = \left(1 - (\alpha - 1) \frac{\pi^2}{6} \left(\frac{T}{\epsilon_F} \right)^2 + \dots \right) \epsilon_F \quad (309)$$

For "spinless" non-relativistic fermions in 3D we have

$$N = V \frac{1}{6\pi^2} (2m)^{\frac{3}{2}} \mu^{\frac{3}{2}} \left(1 + \frac{\pi^2}{8} \left(\frac{T}{\mu} \right)^2 + \dots \right) \quad (310)$$

$$E = V \frac{3}{5} \frac{1}{6\pi^2} (2m)^{\frac{3}{2}} \mu^{\frac{5}{2}} \left(1 + \frac{5\pi^2}{8} \left(\frac{T}{\mu} \right)^2 + \dots \right) \quad (311)$$

leading to

$$\epsilon_F = \frac{1}{2m} \left(6\pi^2 \frac{N}{V} \right)^{\frac{2}{3}} \quad (312)$$

$$\mu = \left(1 - \frac{\pi^2}{12} \left(\frac{T}{\epsilon_F} \right)^2 + \dots \right) \epsilon_F \quad (313)$$

$$E = \left(1 + \frac{5\pi^2}{12} \left(\frac{T}{\epsilon_F} \right)^2 + \dots \right) \frac{3}{5} N \epsilon_F \quad (314)$$

Note that in zero temperature, the pressure given by the equation

$$P = \frac{1}{5} (6\pi^2)^{\frac{2}{3}} \frac{1}{m} \left(\frac{N}{V} \right)^{\frac{5}{3}} \quad (315)$$

Systems with interactions

[7] General perspective

Energy scales.— With regard to the prototype models of systems with interactions there are generically two energy scales. One is the interaction strength ε , and the other is the temperature T . For $T \gg \varepsilon$ a perturbative treatment is appropriate. See below the cluster expansion. For $T \ll \varepsilon$ it is advised to re-model the system with Hamiltonian that describes its collective excitations. The interesting regime is $T \sim \varepsilon$ where the phase transition takes place.

Models of interest.— It is natural to start with the discussion of gas-liquid phase transition and to realize that its "lattice gas" version is formally equivalent to "Ising model" that describes a ferromagnetic phase transition. Its generalization is known as the "Potts model". The system consists of \mathcal{N} sites. At each site there is a "spin" that can be in one of s possible states. The Ising model is a special case with $s = 2$, and the interaction is $\sigma_i \sigma_j$, where $\sigma = \pm 1$. The "Ising model" has a discrete up/down symmetry. Its Field theory version is known as the Landau-Ginzburg model. The Heisenberg model is a different lattice model that has $S_i \cdot S_j$ interaction. This interaction has a continuous symmetry with respect to rotations. Its 2D version is known as the XY model. There are also corresponding Field theory models that are known as non-linear sigma models.

First order phase transition.— There are systems where there are (say) two families of states, such that each family has different DOS with different minimum. In such case a control parameter (call it h) might induce a crossover from the dominance of one family to the dominance of the second family. This crossover is reflected in the partition function and hence in the heat capacity and in the state equations. In the thermodynamic limit the crossover might be abrupt. In such case it is a "first order phase transition". If a change in a parameter leads to a *bifurcation* in the calculation of the partition function, it is called a "second order phase transition". The prototype example for phase transition is ferromagnetism where the magnetization might be "up" or "down".

Order parameter.— In order to analyze a second order phase transition it is useful to identify the "order parameter", which is a field $\varphi(x)$ that describes the coarse grained state of the system. In the prototype example of ferromagnetism it is the magnetization density in the sample. Defining an entropy functional $S[\varphi]$ that reflects the number of microscopic states that have the same field configuration, we can express the partition function as

$$Z = \sum_{\varphi} e^{-A[\varphi]}, \quad A[\varphi] = \frac{1}{T} [E[\varphi] - TS[\varphi]] \quad (316)$$

Symmetry breaking.— Second order phase transition is due spontaneous symmetry breaking leading to long range order. At $T = 0$ the definition of symmetry breaking is very simple. It means that $E[\varphi]$ attains (say) two distinct minimum that are described by different field configurations (different "order"). However, at finite temperature the canonical state is not the minimum of the energy functional $E[\rho]$ but of the free energy functional $F[\rho] = E[\rho] - TS[\rho]$. Accordingly entropic contribution may wash away the broken symmetry.

There is an implicit assumption with regard to the possibility to observe "symmetry breaking". It is assumed that $\varphi(x)$ has slow dynamics. If a magnet is prepared (say) with "up" magnetization then it takes a huge time until it flips to the quasi degenerate "down" magnetization.

Long range order.— In the prototype examples at high temperatures there is no "order" meaning that the correlation function $g(r) = \langle \varphi(r) \varphi(0) \rangle$ decays exponentially. As the critical temperature is approached from above the correlation length diverges. Below the critical temperature there is "long range order" and the correlation function should be re-defined with respect to the new order. There is a possibility to witness "infinite order phase transition" where below the critical temperature there is no long range order, but instead the correlation function become powerlaw. See discussion of the XY model.

Formal analysis.— Disregarding a few models that possess exact solutions, the analysis of the partition function can be done by adopting the following stages: (1) Primitive mean field theory evaluates the partition function by calculating $A[\varphi]$ for the field configuration that minimizes it. This corresponds mathematically to an inferior saddle point approximation. (2) Proper mean field theory is based on proper saddle point approximation, which means that the calculation takes into account the Gaussian fluctuations around the minimum. (3) Renormalization Group (RG) treatment is required in the critical regime, whenever the Gaussian approximation is not valid. It explains the scaling anomalies that are witnessed in the vicinity of the critical temperature.

===== [7.1] Gas of weakly interacting particles

Consider a classical gas of interacting particles:

$$\mathcal{H} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \sum_{\langle ij \rangle} u(\vec{x}_i - \vec{x}_j) \quad (317)$$

The partition function without the Gibbs factor is

$$Z_N(\beta, V) = \left(\frac{1}{\lambda_T^3} \right)^N \int dx_1 \dots dx_N \exp \left[-\beta \sum_{\langle ij \rangle} u(x_{ij}) \right] \quad (318)$$

$$\equiv \left(\frac{1}{\lambda_T^3} \right)^N \int dx_1 \dots dx_N \prod_{\langle ij \rangle} (1 + f(x_{ij})), \quad f(r) \equiv e^{-\beta u(r)} - 1 \quad (319)$$

Note that the configuration space integral has the dimensions of V^N . It equals V^N if there are no interaction. If there are interactions we can regard the $f(r)$ as a perturbation. Then we get an expansion

$$Z_N(\beta, V) = \left(\frac{V}{\lambda_T^3} \right)^N \left[1 + \text{coef}_2 \left(\frac{N}{V} \right) + \text{coef}_3 \left(\frac{N}{V} \right)^2 + \dots \right] \quad (320)$$

From here we can derive the so called Virial expansion for the pressure:

$$P = \frac{NT}{V} \sum_{\ell=1}^{\infty} a_{\ell}(T) \left(\frac{N}{V} \right)^{\ell-1} = \frac{NT}{V} \left[1 + a_2 \left(\frac{N}{V} \right) + a_3 \left(\frac{N}{V} \right)^2 + \dots \right] \quad (321)$$

The a_{ℓ} are known as the virial coefficients. Note that the leading order virial expansion is consistent with the Van-der-Waals equation of state provided one makes the identification $a_2 = \bar{b} - (\bar{a}/T)$, namely,

$$P \approx \frac{NT}{V - N\bar{b}} - \bar{a} \left(\frac{N}{V} \right)^2 \quad (322)$$

===== [7.2] The Virial coefficients

It is simplest to calculate the Virial coefficients using the grand canonical formalism. From now on the dependence on the temperature is implicit, and we emphasize the dependence on the fugacity z . The grand canonical partition function using the Gibbs prescription is

$$\mathcal{Z}(z) = \sum_{N=0}^{\infty} \frac{1}{N!} Z_N z^N, \quad [\text{Here } Z_N \text{ is defined without Gibbs factor}] \quad (323)$$

For an ideal classical gas all the Z_N are determined by the one-particle partition function, namely $Z_N = Z_1^N$. Accordingly $\ln(\mathcal{Z})$ includes a single term, namely $\ln(\mathcal{Z}) = Z_1 z$. It makes sense to assume that interactions and quantum effects will add higher order terms. Hence we postulate an expansion

$$\ln \mathcal{Z}(z) = \sum_{n=1}^{\infty} \frac{1}{n!} B_n z^n \equiv V \sum_{n=1}^{\infty} b_n(T) \left(\frac{z}{\lambda_T^3} \right)^n \quad (324)$$

where $b_1 = 1$, and b_n has the dimension of length^{n-1} . Note that for an ideal Bose or Fermi gas one obtains $b_\ell = (\pm 1)^{\ell+1} \ell^{-5/2} (\lambda_T^3)^{n-1}$. We would like to find a procedure to determine these coefficients if there are weak interactions between the particles. Once they are known we get the state equations from

$$N = z \frac{\partial}{\partial z} \ln \mathcal{Z} \quad (325)$$

$$P = \frac{T}{V} \ln \mathcal{Z} \quad (326)$$

leading to

$$\frac{N}{V} = \sum_{n=1}^{\infty} n b_n(T) \left(\frac{z}{\lambda_T^3} \right)^n \quad (327)$$

$$\frac{P}{T} = \sum_{n=1}^{\infty} b_n(T) \left(\frac{z}{\lambda_T^3} \right)^n \quad (328)$$

It is customary to eliminate z/λ_T^3 from the first equation and to substitute into the second equation, getting

$$a_1 = b_1 = 1 \quad (329)$$

$$a_2 = -b_2 \quad (330)$$

$$a_3 = 4b_2^2 - 2b_3 \quad (331)$$

It is implied from the discussion in the next section that in order to get b_2 we just have to calculate the two-body partition function Z_2 . Namely:

$$b_2 = V \frac{1}{2!} \left[\frac{Z_2}{Z_1^2} - 1 \right] \quad [\text{no Gibbs prescription here!}] \quad (332)$$

The calculation of Z_2 for two interacting quantum particles, given the scattering phase-shifts, has been outlined in a past lecture. In the classical case it is standard to assume that the gas particles are like hard spheres, each having radius R , with some extra attractive part that has depth $\sim \epsilon_0$, similar to Lenard-Jones potential. Accordingly in leading order

$$b_2 = \frac{1}{2} \int \left[e^{-\beta u(r)} - 1 \right] d^3r \approx -\frac{1}{2} \left[1 - \frac{\epsilon_0}{T} \right] V(2R) \equiv -\left[\bar{b} - \frac{\bar{a}}{T} \right] \quad (333)$$

where $V(r)$ is the volume of a sphere that has radius r . This gives interpretation for the phenomenological constants \bar{a} and \bar{b} in the Van-der-Waals equation of state. In particular note that \bar{b} is the excluded volume multiplied by 2^{d-1} , where $d = 3$. Contrary to a common misconception it is only in 1D that \bar{b} equals the excluded volume.

===== [7.3] The cluster expansion

Our objective is to calculate the b_n coefficients. These are scaled versions of the coefficients B_n in the expansion of $\ln(\mathcal{Z})$, and they are related to the coefficients Z_N in the expansion of \mathcal{Z} . The relation between them is formally the same as the relation between cumulants and moments in probability theory:

$$Z_1 = B_1 \quad (334)$$

$$Z_2 = B_1^2 + B_2 \quad (335)$$

$$Z_3 = B_1^3 + 3B_1 B_2 + B_3 \quad (336)$$

Or backwards:

$$B_1 = Z_1 \quad (337)$$

$$B_2 = Z_2 - Z_1^2 \quad (338)$$

$$B_3 = Z_3 - 3Z_2Z_1 + 2Z_1^3 \quad (339)$$

We can use these relations both directions: First we can evaluate a few Z_N , typically Z_1 and Z_2 , in order to get the leading order B_n coefficients, say B_1 and B_2 . Once the leading order B_n coefficients are known, we can generate from them a generalized Gibbs approximation for all(!) the Z_N .

Diagrammatic procedure.— We turn to outline a general diagrammatic procedure to evaluate the b_ℓ for a classical gas of interacting particles. A graph (network, diagram) is a set of vertices (nodes) that are connected by edges (connectors, bonds). In the present context each diagram represents an integral. The sum over all the connected diagrams that have n nodes gives the expansion coefficient B_n of the "comulant" generating function $\ln(\mathcal{Z})$, while the sum over all diagrams (including reducible diagrams) gives the expansion coefficient Z_N of the "moment" generating function \mathcal{Z} . Formally we write

$$Z_N = \left(\frac{1}{\lambda_T^3} \right)^N \int dx_1 \dots dx_N \prod_{\langle ij \rangle} (1 + f(x_{ij})) = \left(\frac{1}{\lambda_T^3} \right)^N \sum [\text{diagrams with } N \text{ nodes}] \quad (340)$$

In this expression a diagram represents an integral of the type

$$C[3', 1, 2, 3] \times \int [f(x_{12})f(x_{23})] [f(x_{56})] [f(x_{78})f(x_{89})f(x_{97})] dx_1 \dots dx_9 \quad (341)$$

where C is a combinatorial factor that arise because we identify diagrams that differ only in the labeling of the vertices. One should realize that if a diagram is reducible, say $N = n_1 + n_2 + n_3$, then $C[n_1, n_2, n_3] = [N!/(n_1!n_2!n_3!)]C[n_1]C[n_2]C[n_3]$. In the above example $C[3'] = 3$ is the number of ways to have a triangle with 2 bonds, while $C[3] = 1$. Using this observation it is not difficult to prove that

$$B_n = \left(\frac{1}{\lambda_T^3} \right)^n \sum [\text{connected diagrams with } n \text{ nodes}] \quad (342)$$

The expression for the b_n with prefactor $1/(n!V)$ is implied. The expressions for the leading coefficients are:

$$b_1 = \frac{1}{V} \int dx = 1 \quad (343)$$

$$b_2 = \frac{1}{2!V} \int f(x_{12}) dx_1 dx_2 = \frac{1}{2!} \int f(r) dr \quad (344)$$

$$b_3 = \frac{1}{3!V} \int [3f(x_{12})f(x_{23}) + f(x_{12})f(x_{23})f(x_{31})] dx_1 dx_2 dx_3 \quad (345)$$

===== [7.4] From gas with interaction to Ising problem

Consider classical gas with interactions $U(\vec{r}_1, \dots, \vec{r}_N)$. The N particle partition function is

$$Z_N = \frac{1}{N!} \left(\frac{1}{\lambda_T} \right)^{3N} \int d^{3N}r e^{-\beta U(r_1, \dots, r_N)} \quad (346)$$

We see that the kinetic part factors out, hence the whole physics of the interactions is in the configuration integral. Therefore, without loss of generality we can consider "static gas". To further simplify the treatment we consider a

”lattice gas” version:

$$\mathcal{H} = U(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{2} \sum_{x, x'} u(x, x') n(x) n(x') \quad (347)$$

The grand partition function is

$$\mathcal{Z} = \sum_{n(\cdot)} \exp \left[-\beta \left(\frac{1}{2} \sum_{x, x'} u(x, x') n(x) n(x') - \mu \sum_x n(x) \right) \right] \quad (348)$$

where $n(x) = 0, 1$. We define

$$n(x) = \frac{1 + \sigma(x)}{2} \quad (349)$$

where $\sigma(x) = \pm 1$. Then we get

$$\mathcal{Z} = \sum_{\sigma(x)} \exp \left[-\beta \left(\sum_{\langle x, x' \rangle} \varepsilon(x, x') \sigma(x) \sigma(x') - h \sum_x \sigma(x) + \text{const} \right) \right] \quad (350)$$

where $\varepsilon = u/4$, and $h = [\mu - \bar{u}]/2$. Here \bar{u} is the interaction energy per site for full occupation. Note that $h = 0$ implies that a fully occupied lattice has the same energy as an empty lattice. We represent graphically the interaction $\varepsilon(x, x')$ between two sites x and x' by “bonds”. The notation $\langle x, x' \rangle$ means from now on summation over all the bonds without double counting. In the simplest case there are interactions only between near-neighbor sites.

We see that the calculation of \mathcal{Z} for static lattice gas is formally the same as calculation of Z for an Ising model. The following analogies should be kept in mind

$$\text{occupation } N \longleftrightarrow \text{magnetization } M = 2N - \mathcal{N} \quad (351)$$

$$\text{chemical potential } \mu \longleftrightarrow \text{magnetic field } h \quad (352)$$

$$\text{fugacity } z = e^{\beta\mu} \longleftrightarrow \text{define } z = e^{2\beta h} \quad (353)$$

$$\text{grand canonical } \mathcal{Z}(\beta, \mu) \longleftrightarrow \text{canonical } Z(\beta, h) \quad (354)$$

From now on we refer to Ising model, but for the formulation of some theorems in the next section it is more convenient to use the lattice gas language for heuristic reasons. Note also that N is more convenient than M because it does not skip in steps of 2.

===== [7.5] Yang and Lee theorems

Consider the lattice gas or the equivalent Ising model. The probability of a given configuration is

$$P_R \propto [e^{-\beta E_R}] z^{N_R} \quad (355)$$

where E_R is the energy of the interactions, and z is the fugacity. The partition function is

$$\mathcal{Z}(z; \beta) = \sum_{N=0}^{\mathcal{N}} \mathcal{Z}_N(\beta) z^N \quad (356)$$

The Helmholtz function is

$$F(z; \beta) = -\frac{1}{\beta} \ln \mathcal{Z}(z; \beta) \quad (357)$$

The expectation value of the total magnetization is

$$\langle N \rangle = -\beta z \frac{\partial}{\partial z} F(z; \beta) \quad (358)$$

As we increase z we expect the magnetization $\langle N \rangle$ to grow. We expect $\langle N \rangle / \mathcal{N}$ to have a well defined value in the limit $\mathcal{N} \rightarrow \infty$. Moreover, below some critical temperature we expect to find a phase transition. In the latter case we expect $\langle N \rangle$ to have a jump at zero field ($z = 1$). The Yang and Lee theorems formulate these expectations in a mathematically strict way.

Given \mathcal{N} it is clear that we can write the polynomial \mathcal{Z} as a product over its roots:

$$\mathcal{Z}(z) = \text{const} \times \prod_{r=1}^{\mathcal{N}} (z - z_r) \quad (359)$$

Consequently

$$F(z) = -\frac{1}{\beta} \sum_{r=1}^{\mathcal{N}} \ln(z - z_r) + \text{const} \quad (360)$$

and

$$\langle N \rangle = z \sum_{r=1}^{\mathcal{N}} \frac{1}{z - z_r} \quad (361)$$

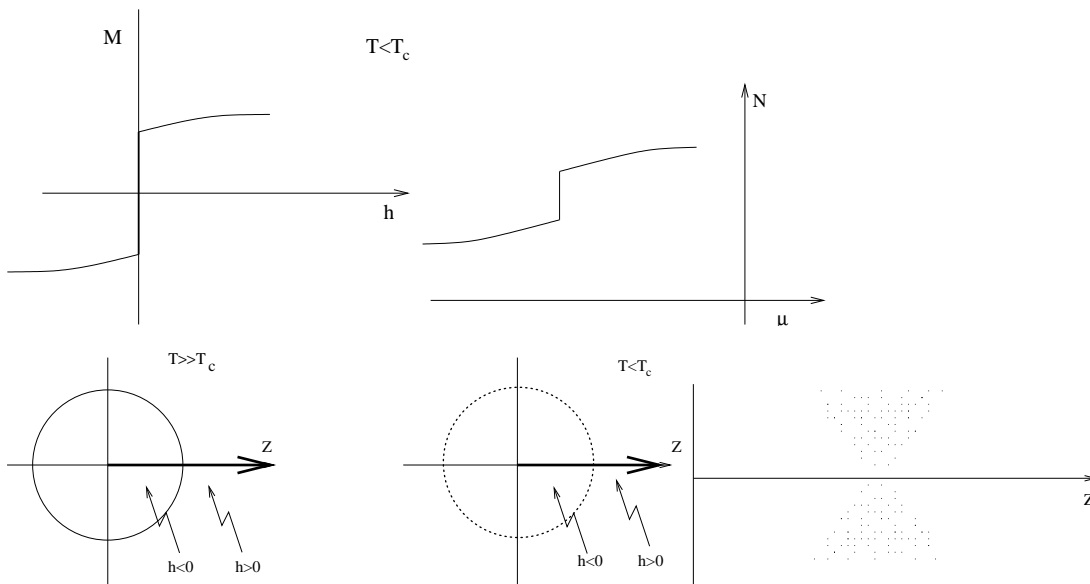
There is a strict analogy here with the calculation of an electrostatic field in a 2D geometry. In the absence of interactions (infinite temperature) we get that all the roots are at $z = -1$. Namely,

$$\mathcal{Z}(z; \beta) = \sum_{N=0}^{\mathcal{N}} C_{\mathcal{N}}^N z^N = (1 + z)^{\mathcal{N}} \quad (362)$$

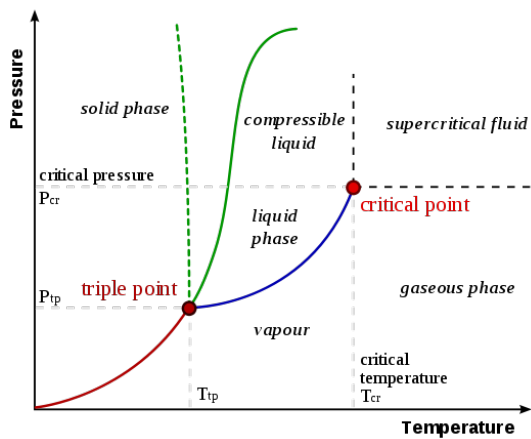
So we do not have phase transition since the physical axis is $0 < z < 1$, where this function is analytic. The questions are what happens to the distribution of the roots as we increase the interaction (lower the temperature), and what is the limiting distribution in the thermodynamics limit ($\mathcal{N} \rightarrow \infty$). There are three statements that give answers to these questions due to Yang and Lee. The first statement is regarding the existence of the thermodynamics limit:

$$\lim_{\mathcal{N} \rightarrow \infty} \frac{F(z)}{\mathcal{N}} = \text{exists} \quad (363)$$

The second statement relates specifically to the standard Ising model, saying that all the roots are lying on the circle $|z_r| = 1$. In general other distributions are possible. The third statement is that below the critical temperature the density of roots at $z = 1$ becomes non-zero, and hence by Gauss law $\langle N \rangle / \mathcal{N}$ has a jump at zero field. This jump is discontinuous in the thermodynamic limit.



In the (T, μ) phase diagram the discontinuity is indicated by a solid line that stretch from $(0, \bar{u})$ to (T_c, \bar{u}) . However in practice it is customary to use a (T, P) phase diagram. Here we bring the phase diagram of water as an example [Wikipedia]:



In the grand-canonical perspective N as a function of μ exhibits a jump at $\mu = \bar{u}$. In the canonical perspective we fix N and solve for μ . Then we get a "gas" or a "liquid" state provided the N line does not intersect the discontinuity. Otherwise there is a phase separation, where the gas and the liquid phases coexist with the same chemical potential $\mu = \bar{u}$.

[8] The Ising model

===== [8.1] Model definition

The energy of a given Ising model configuration state is

$$E[\sigma(\cdot)] = - \sum_{\langle x, x' \rangle} \varepsilon(x, x') \sigma(x) \sigma(x') - \sum_x h(x) \sigma(x) \quad (364)$$

The canonical state is

$$p[\sigma(\cdot)] = \frac{1}{Z} e^{-\beta E[\sigma(\cdot)]} \quad (365)$$

where the partition function is

$$Z[h(\cdot), \beta] = \sum_{\sigma(\cdot)} \exp \left[\beta \left(\sum_{\langle x, x' \rangle} \varepsilon(x, x') \sigma(x) \sigma(x') + \sum_x h(x) \sigma(x) \right) \right] \quad (366)$$

We expand the Helmholtz function as

$$F[h(\cdot), T] = F_0(T) - \frac{1}{2T} \sum_{x, x'} g(x, x') h(x) h(x') + \mathcal{O}(h^4) \quad (367)$$

From here we get

$$\langle \sigma(x) \rangle = - \frac{\partial F}{\partial h(x)} = \frac{1}{T} \sum_{x'} g(x, x') h(x') \quad (368)$$

$$\langle \sigma(x) \sigma(x') \rangle_0 = -T \left. \frac{\partial F}{\partial h(x) \partial h(x')} \right|_0 = g(x, x') \quad (369)$$

for an homogeneous field we replace $F[h(\cdot), T]$ by $F(h, T)$ and we get

$$\tilde{M} = - \frac{\partial F}{\partial h} = N \chi h + \mathcal{O}(h^3) \quad (370)$$

with the "fluctuation-response relation"

$$\chi = \frac{1}{T} \sum_r g(r) \quad (371)$$

Unless indicted explicitly otherwise $F(T)$ is calculated for zero field. We have the usual expressions:

$$E(T) = F(T) + TS(T) \quad (372)$$

$$S(T) = - \frac{\partial F(T)}{\partial T} \quad (373)$$

$$C(T) = T \frac{\partial S}{\partial T} = \frac{dE}{dT} \quad (374)$$

===== [8.2] The spatial correlation function

It is possible to measure $g(r)$ via a scattering experiment. Given a configuration $\sigma(x)$ the intensity of the scattering in the Born approximation is

$$I(q) \propto \left| \int \sigma(x) e^{-i\vec{q} \cdot \vec{x}} d\vec{x} \right|^2 \quad (375)$$

If we average over configurations we get

$$I(q) \propto \int dx dx' \langle \sigma(x) \sigma(x') \rangle e^{-iq \cdot (\vec{x} - \vec{x}')} \propto \tilde{g}(q) \quad (376)$$

where $\tilde{g}(q)$ is the FT of the correlation function. We shall see that Landau's approach in the Gaussian approximation leads to the Ornstein-Zernike expression

$$\tilde{g}(q) \propto \left(\frac{1}{q^2 + (1/\xi)^2} \right) \quad (377)$$

This leads to

$$g(r) \sim \exp(-r/\xi) \quad \text{if } \xi < \infty \quad (378)$$

$$g(r) \sim 1/r^{d-2} \quad \text{if } \xi = \infty \quad (379)$$

The information about order-disorder transition is in $g(r)$. If $\xi < \infty$ there is no long range order, and we get

$$\chi = \frac{1}{T} \sum_r g(r) < \infty \quad (380)$$

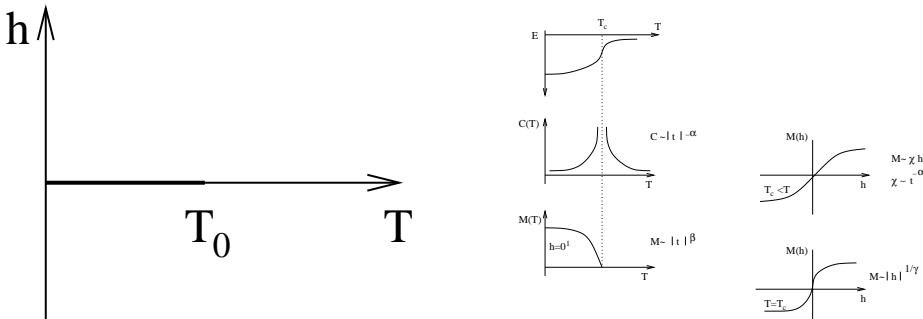
as $\xi \rightarrow \infty$ the susceptibility diverges which suggests spontaneous magnetization as phase transition. Below the critical temperature one should define the correlation function as follows:

$$g(r) \equiv \langle \sigma(x) \sigma(x') \rangle - \langle \sigma(x) \rangle^2 \quad (381)$$

where $r = |x - x'|$.

===== [8.3] Critical behavior and the scaling hypothesis

Below we display the phases diagram in (T, h) space, and qualitative plots of the state equations. For the 2D Ising model with near neighbor interactions $T_c = 2.27\epsilon$.



The state equations in the critical region are characterized by the exponents $\alpha, \beta, \gamma, \delta$ (see below). Two other exponents ν and η are defined via the critical behavior of the correlation function, which is assumed to be a variation on the Ornstein-Zernike expression. Namely, one conjectures that the divergence of the correlation length as $T \rightarrow T_c$ is described by

$$\xi \sim |T - T_c|^{-\nu} \quad (382)$$

and that the correlation function is

$$g(r) \sim \frac{1}{r^{d-2+\eta}} \exp(-r/\xi) \quad (383)$$

Here we combined the $T = T_c$ and the $T > T_c$ into one expression. This expression describes the long range behavior. Note that the "microscopic" short range behavior is not too interesting because it is bounded by $g(0) = 1$. The divergence of χ is due to the slow power-law tails. Below T_c the behavior is similar to $T > T_c$ provided the correlation function is properly defined. Going on with the same phenomenology the conjecture is that away from T_c the correlation distance ξ is the only relevant length scale in the thermodynamic limit. This means that each "correlated block" of the system has the same contribution to the Free energy irrespective of the temperature, hence

$$F_0(T) \sim \frac{V}{\xi^d} \propto |T - T_c|^{-\nu d} \quad (384)$$

where d is the dimensionality. It is customary to define the scaled temperature as $t = |T - T_c|/T_c$, and to summarize the above conjectures as a *scaling hypothesis* that involves the critical exponents:

$$F_0(s^{-1/\nu}t) = s^{-d}F_0(t) \quad (385)$$

$$g(sr, s^{-1/\nu}t) = s^{-(d-2+\eta)}g(r, t) \quad (386)$$

From here it follows that

$$C(s^{-1/\nu}t) = s^{(2/\nu)-d}C(t) \quad (387)$$

$$\chi(s^{-1/\nu}t) = s^{2-\eta}\chi(t) \quad (388)$$

From the combined scaling relation

$$F\left(s^{-1/\nu}t, s^{-(d+2-\eta)/2}h\right) = s^{-d}F(t, h) \quad (389)$$

we can deduce similar relations for the magnetization. These scaling relations allow to deduce the critical exponents $\alpha, \beta, \gamma, \delta$ from d, ν, η , leading to

$$C \sim |t|^{-\alpha}, \quad \alpha = 2 - \nu d \quad (390)$$

$$M \sim |t|^\beta, \quad \beta = (d - 2 + \eta)\nu/2 \quad (391)$$

$$\chi \sim t^{-\gamma}, \quad \gamma = (2 - \eta)\nu \quad (392)$$

$$M \sim |h|^{1/\delta}, \quad \delta = (d + 2 + \eta)/(d - 2 + \eta) \quad (393)$$

The so called "classical" mean-field exponents that we derive later are

$$\nu = 1/2, \quad \eta = 0, \quad \alpha = 0, \quad \beta = 1/2, \quad \gamma = 1, \quad \delta = 3 \quad (394)$$

In order to get a non-trivial result for α we have to take into account Gaussian fluctuations around the mean field leading to $\alpha = [2 - (d/2)]$. One observes that the classical mean-field exponents satisfy the scaling hypothesis based

relations if $d = 4$, but not for $d = 3$. This implies that we have to go beyond mean field theory in order to establish the experimentally observed scaling behavior.

===== [8.4] Digression regarding scaling

A function of one variable has a scaling property if

$$F(sx) = s^{D_F} F(x) \quad (395)$$

where D_F is the scaling exponent. It follows that $F(x) = \text{const } x^{D_F}$. For example $F(x) = x^2$ has the scaling exponent $D_F = 2$. If we have say two variables then the more general definition is

$$F(s^{D_x} x, s^{D_y} y) = s^{D_F} F(x, y) \quad (396)$$

Note that the scaling exponents can be multiplied by the same number, and still we have the same scaling relation. It follows that there is a scaling function such that

$$F(x, y) = y^{D_F/D_y} f\left(\frac{x}{y^{D_x/D_y}}\right) \quad (397)$$

For example $F(x, y) = x^2 + y^3$ has the scaling exponents $D_x = 1/2, D_y = 1/3, D_F = 1$. More generally any “physical” function has an “engineering” scaling property that follows trivially from dimensional analysis.

===== [8.5] Solution of the 1D Ising Model

Assuming only near neighbor interactions

$$E[\sigma] = -\varepsilon \sum_{\langle ij \rangle} \sigma_i \sigma_j - \sum_i h_i \sigma_i \quad (398)$$

The partition function is

$$Z[h, \beta] = \sum_{\sigma(\cdot)} e^{-\beta E[\sigma]} \quad (399)$$

For $\varepsilon = 0$ we get

$$Z[h, \beta] = \prod_{i=1}^N 2 \cosh(\beta h_i) \quad (400)$$

and hence

$$F[h, T] = -T \sum_{i=1}^N \ln \left(2 \cosh \left(\frac{h_i}{T} \right) \right) \approx -NT \ln(2) - \frac{1}{2T} \sum_{i=1}^N h_i^2 \quad (401)$$

The correlation function is

$$g(r) = -T \frac{\partial F}{\partial h_i \partial h_j} = \delta_{ij} = \delta_{r,0} \quad (402)$$

and hence the susceptibility is

$$\chi = \frac{1}{T} \sum_r g(r) = \frac{1}{T} \quad (403)$$

The magnetization is

$$\tilde{M} = -\frac{\partial F}{\partial h} = N \tanh\left(\frac{h}{T}\right) \approx N\chi h + \mathcal{O}(h^3) \quad (404)$$

We turn now to the case $\varepsilon \neq 0$ and assume homogeneous field h . This allows to use the transfer matrix method for solutions. Let us define the scaled parameters

$$\tilde{\varepsilon} \equiv \beta\varepsilon \quad (405)$$

$$\tilde{h} \equiv \beta h \quad (406)$$

and the matrix

$$T_{\sigma'\sigma''} \equiv \exp\left[\tilde{\varepsilon}\sigma'\sigma'' + \frac{1}{2}\tilde{h}(\sigma' + \sigma'')\right] = \begin{pmatrix} e^{\tilde{\varepsilon}+\tilde{h}} & e^{-\tilde{\varepsilon}} \\ e^{-\tilde{\varepsilon}} & e^{\tilde{\varepsilon}-\tilde{h}} \end{pmatrix} \quad (407)$$

The eigenvalues of this matrix are

$$\lambda_{\pm} = e^{\tilde{\varepsilon}} \cosh(\tilde{h}) \pm e^{-\tilde{\varepsilon}} \sqrt{1 + e^{4\tilde{\varepsilon}} \sinh^2(\tilde{h})} \quad (408)$$

The partition function of \mathcal{N} site Ising model on a ring can be calculated as

$$Z(\beta, h) = \text{trace}(T^{\mathcal{N}}) = \lambda_+^{\mathcal{N}} + \lambda_-^{\mathcal{N}} \quad (409)$$

and hence for very large \mathcal{N} we get

$$F(T, h) = -\mathcal{N}T \ln(\lambda_+) \quad (410)$$

Expanding we get

$$F(T, h) \approx -\mathcal{N}T \ln\left(2 \cosh\left(\frac{\varepsilon}{T}\right)\right) - \frac{1}{2}\mathcal{N} \frac{\exp\left(2\frac{\varepsilon}{T}\right)}{T} h^2 \quad (411)$$

Hence

$$\chi = \frac{1}{T} \exp\left(2\frac{\varepsilon}{T}\right) \quad (412)$$

Now we would like to calculate the correlation function at zero field.

$$g(r) \equiv \langle \sigma_0 \sigma_r \rangle = \frac{1}{Z} \sum_{\sigma_0 \sigma_r} \sigma_0 T_{\sigma_0 \sigma_r}^r \sigma_r T_{\sigma_r \sigma_0}^{\mathcal{N}-r} \quad (413)$$

We have

$$T_{\sigma, \sigma''} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \quad (414)$$

with

$$\lambda_+ = 2 \cosh(\tilde{\varepsilon}) \quad (415)$$

$$\lambda_- = 2 \sinh(\tilde{\varepsilon}) \quad (416)$$

Using standard Pauli matrix notations and denoting the digonalized matrix T as Λ we get

$$g(r) = \frac{1}{Z} \text{trace} [\sigma_z T^r \sigma_z T^{\mathcal{N}-r}] = \frac{1}{Z} \text{trace} [\sigma_x \Lambda^r \sigma_x \Lambda^{\mathcal{N}-r}] = \frac{\lambda_+^r \lambda_-^{\mathcal{N}-r} + \lambda_-^r \lambda_+^{\mathcal{N}-r}}{\lambda_+^{\mathcal{N}} + \lambda_-^{\mathcal{N}}} \quad (417)$$

For very large \mathcal{N} we get

$$g(r) = \left(\frac{\lambda_-}{\lambda_+} \right)^r = e^{-r/\xi} \quad (418)$$

where

$$\xi = \left[\ln \left(\coth \left(\frac{\varepsilon}{T} \right) \right) \right]^{-1} \approx e^{2\varepsilon/T} \quad (419)$$

The calculation of $\sum g(r)$ involves a geometric summation, and it can be verified that it equals ξ . The result is as expected in agreement with what we got for χ .

===== [8.6] Solution of the 2D Ising model

The full details of the Onsager solution for this problem is in Huang. Also here the transfer matrix approach is used. Recall that the zero field solution of the 1D model is

$$\frac{1}{\mathcal{N}} \ln Z = \ln(2) + \ln(\cosh(\tilde{\varepsilon})) \quad (420)$$

The 2D solution is

$$\frac{1}{\mathcal{N}} \ln Z = \ln(2) + \frac{1}{2} \int \int \frac{d\theta d\theta'}{(2\pi)^2} \ln \left[(\cosh(2\tilde{\varepsilon}))^2 + \sinh(2\tilde{\varepsilon}) (\cos \theta + \cos \theta') \right] \quad (421)$$

The integral is determined by the dimensionless parameter

$$\kappa \equiv \frac{2 \sinh(2\tilde{\varepsilon})}{(\cosh(2\tilde{\varepsilon}))^2} \leq 1 \quad (422)$$

The value $\kappa = 1$, for which $\ln Z$ exhibits discontinuity in its derivative, is attained for $\sinh(\tilde{\varepsilon}) = 1$, from which it follows that the critical value of the interaction is $\tilde{\varepsilon} = 0.44$, leading to $T_c = 2.27\varepsilon$. This is close to the heuristic value $T_c \approx 2\varepsilon$ that we are going to derive in the next lecture.

[9] Phase transitions - heuristic approach

===== [9.1] The ferromagnetic phase transition

The standard Ising Hamiltonian is

$$\mathcal{H} = -\varepsilon \sum_{\langle ij \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i \quad (423)$$

Let us assume that in equilibrium we can regard the spins as quasi-independent, each experiencing an effective field \bar{h} , such that the effective Hamiltonian for the spin at site i is $\mathcal{H}^{(i)} = -\bar{h}\sigma_i$. This means that the equilibrium state is

$$p_{\sigma_1 \dots \sigma_N} \propto \exp \left[-\beta \bar{h} \sum_i \sigma_i \right] \quad (424)$$

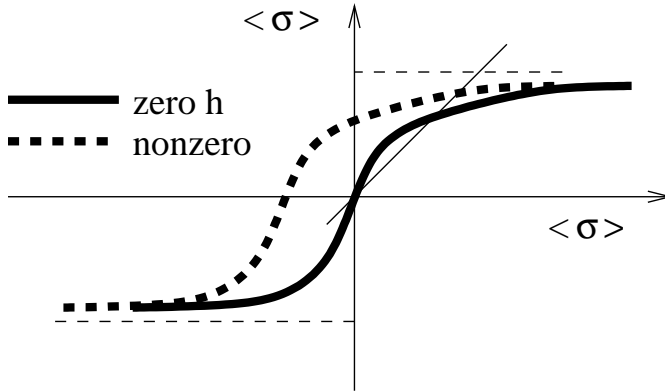
We have to find what is \bar{h} . The formal way is to use a variational scheme. We shall introduce this procedure later. In this section we guess the result using a self-consistent picture. By inspection of the Hamiltonian if the mean magnetization of each spin is $\langle \sigma \rangle$, then it is reasonable to postulate that

$$\bar{h} = h + \varepsilon \sum_{\text{neighbors}} \langle \sigma_j \rangle = h + c\varepsilon \langle \sigma \rangle \quad (425)$$

where c is the coordination number. Form $\mathcal{H}^{(i)}$ we get the self-consistent requirement

$$\langle \sigma \rangle = \tanh \left(\frac{1}{T} (h + c\varepsilon \langle \sigma \rangle) \right) \quad (426)$$

This equation should be solved for $\langle \sigma \rangle$, and then we get \bar{h} as well.



By inspection of the plot we observe that for $h = 0$ the condition for getting a non trivial solution is $c\varepsilon/T > 1$. Therefore $T_c = c\varepsilon$. If we want to explore the behavior in the critical region it is convenient to re-write the equation in the following way:

$$h = T \tanh^{-1} \langle \sigma \rangle - T_c \langle \sigma \rangle \quad (427)$$

and to approximate it as

$$h = (T - T_c) \langle \sigma \rangle + \frac{1}{3} T_c \langle \sigma \rangle^3 \quad (428)$$

for $T > T_c$ we get the Curie-Weiss law

$$\langle \sigma \rangle = \frac{1}{T - T_c} h \quad (429)$$

hence we get the critical exponent $\gamma = 1$. For $T = T_c$ we get

$$\langle \sigma \rangle = \left(\frac{3}{T_c} h \right)^{\frac{1}{3}} \quad (430)$$

hence we get the critical exponent $\delta = 3$. For $T < T_c$ we get

$$\langle \sigma \rangle = \left(3 \frac{T_c - T}{T} \right)^{\frac{1}{2}} \quad (431)$$

hence we get the critical exponent $\beta = 1/2$.

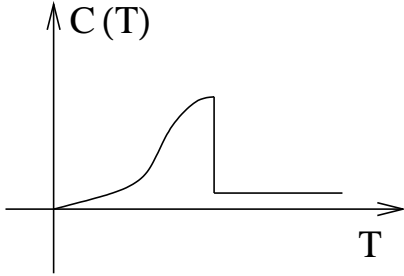
In the mean field approximation the spins are independent of each other, and therefore $\langle \sigma_i \sigma_j \rangle = \langle \sigma_i \rangle \langle \sigma_j \rangle$. It follows that the energy is

$$E = \langle H \rangle = -\frac{1}{2} c \mathcal{N} \varepsilon \langle \sigma \rangle^2 \quad (432)$$

For the heat capacity we get

$$C(T) = \left. \frac{dE}{dT} \right|_{h=0} = -c \varepsilon \mathcal{N} \langle \sigma \rangle \frac{\partial \langle \sigma \rangle}{\partial T} \Big|_{h=0} \quad (433)$$

For $T > T_c$ we get $C(T) = 0$ which implies the critical exponent $\alpha = 0$. To get the non-trivial mean-field result $\alpha = [2 - (d/2)]$ we have to take into account Gaussian fluctuations.



===== [9.2] The anti-ferromagnetic phase transition

The Ising Hamiltonian with $\varepsilon \mapsto -\varepsilon$

$$\mathcal{H} = \varepsilon \sum_{\langle ij \rangle} \sigma_i \sigma_j - h \sum_k \sigma_k \quad (434)$$

We mark the magnetization of the two sub lattices by M_a and M_b . We define

$$M = \frac{1}{2} (M_a + M_b) \quad (435)$$

$$M_s = \frac{1}{2} (M_a - M_b) \quad (436)$$

Without the magnetic field, the problem is the same as the ferromagnetic one with M_s as the order parameter. With magnetic field h the heuristic mean field equations become

$$M_a = \tanh\left(\frac{1}{T}(h - T_c M_b)\right) \quad (437)$$

$$M_b = \tanh\left(\frac{1}{T}(h - T_c M_a)\right) \quad (438)$$

Following the same algebraic simplification procedure as in the ferromagnetic case, we get after addition and subtraction of the two resulting equations,

$$(T - T_c) M_s + \frac{1}{3} T_c (3M^2 M_s + M_s^3) = 0 \quad (439)$$

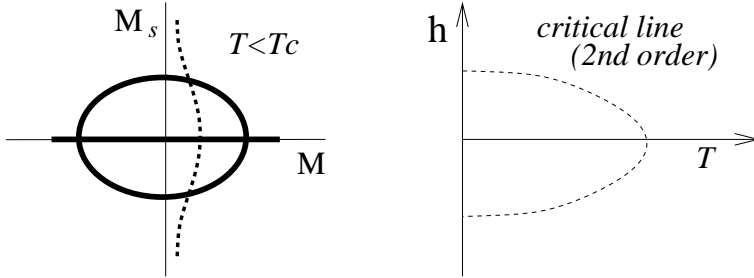
$$(T + T_c) M + \frac{1}{3} T_c (3M_s^2 M + M^3) = h \quad (440)$$

From here it follows that (see graphical illustration):

$$M_s = 0 \quad \text{or} \quad 3M^2 + M_s^2 = 3\left(\frac{T_c - T}{T}\right) \quad (441)$$

$$(2 + M_s^2)M + \frac{1}{3}M^3 = \frac{h}{T_c} \quad (442)$$

As expected from the second equation we get $M = 0$ in the absence of an external field, and from the first equation we get the order parameter $M_s(T)$, which satisfies the same equation as in the ferromagnetic problem. If we switch on the magnetic field T_c is shifted to a lower temperature.



If the magnetic field h is strong enough, it destroys the anti-ferromagnetic order and causes $M_s = 0$. This is implied by the identification the ground state:

$$E(\uparrow\downarrow\uparrow\downarrow) = \mathcal{N} \cdot \left(-\frac{1}{2}c\epsilon\right), [\text{for weak field}] \quad (443)$$

$$E(\uparrow\uparrow\uparrow\uparrow) = \mathcal{N} \cdot \left(\frac{1}{2}c\epsilon - h\right), [\text{for strong field}] \quad (444)$$

In the region where $T \sim T_c$ and $h \sim 0$ we get for the magnetization

$$M = \left(\frac{1}{T_c + T\left(1 + \frac{1}{6}M_s(T)^2\right)}\right) h \equiv \chi h \quad (445)$$

We can get a better general expression for all of the temperature range by differentiation of the heuristic equations

$$\chi = \frac{1}{T_c + T \cosh^2\left(\frac{T_c}{T}M_s(T)\right)} \quad (446)$$

In the region $T \sim T_c$ substitution of $M_s(T)$ gives

$$\chi = \begin{cases} \frac{1}{T_c + T} & T_c < T \\ \frac{1}{4T_c - 2T} & T < T_c \end{cases} \quad (447)$$

===== [9.3] The variational approach

The canonical state minimizes the Free energy functional. Accordingly we look for a solution to the variation problem

$$F[\rho] \equiv \langle H \rangle - TS[\rho] = \text{minimum} \quad (448)$$

with implicit constraint on the normalization. In the mean-field approach the canonical state is assumed to be well approximated by $\rho = \{p_\sigma\}$, where

$$p_{\sigma_1 \dots \sigma_N} = \frac{1}{(2 \cosh(\beta \bar{h}))^N} \exp \left[-\beta \bar{h} \sum_k \sigma_k \right] \quad (449)$$

Here the variational parameter \bar{h} is the effective mean field. We would like to determine the optimal value of \bar{h} for which $F[\rho]$ is minimal. For the calculation we use the identity $F[\rho] = F_0[\rho] + \langle H - H_0 \rangle$, where $H_0 = -\bar{h} \sum_i \sigma_i$, leading to

$$F[\rho] = \mathcal{N} \left[-T \ln \left(2 \cosh \left(\frac{\bar{h}}{T} \right) \right) - \frac{1}{2} c \epsilon \left(\tanh \left(\frac{\bar{h}}{T} \right) \right)^2 - (h - \bar{h}) \tanh \left(\frac{\bar{h}}{T} \right) \right] \quad (450)$$

The variational equation for \bar{h} is as expected

$$\bar{h} = h + c \epsilon \tanh \left(\frac{\bar{h}}{T} \right) \quad (451)$$

Hence, we get the variational free energy

$$F(T, h) = \mathcal{N} \left[-T \ln \left(2 \cosh \left(\frac{\bar{h}}{T} \right) \right) + \frac{1}{2} c \epsilon \left(\tanh \left(\frac{\bar{h}}{T} \right) \right)^2 \right] \quad (452)$$

and the magnetization

$$\tilde{M} = -\frac{\partial F(T, h)}{\partial h} = -\frac{\partial F}{\partial \bar{h}} \frac{\partial \bar{h}}{\partial h} = \mathcal{N} \tanh \left(\frac{\bar{h}}{T} \right) \quad (453)$$

The above expressions for $F(T, h)$ and $\tilde{M}(T, h)$ are not convenient because the dependence of \bar{h} on h is not explicit. To make calculations of state equations it is convenient to transform to

$$A(T, \tilde{M}) \equiv F(T, h) + h \tilde{M} \quad (454)$$

such that $dA = -SdT + h d\tilde{M}$. In order to make the change of variable we note that from the $\tilde{M}(T, h)$ expression, and from the mean field equation for \bar{h} it follows that

$$h = T \tanh^{-1}(M) - c \epsilon M \quad \text{where } M \equiv \frac{\tilde{M}}{\mathcal{N}} = \langle \sigma \rangle \quad (455)$$

Using the identity $\tanh^{-1}(x) = (1/2) \ln((1+x)/(1-x))$ one obtains

$$A(T, M) = \mathcal{N} \left[-T \ln 2 + \frac{1}{2} T \ln(1 - M^2) + \frac{1}{2} T M \ln \left(\frac{1+M}{1-M} \right) - \frac{1}{2} c \epsilon M^2 \right] \quad (456)$$

$$= \mathcal{N} T \left[\frac{1+M}{2} \ln \frac{1+M}{2} + \frac{1-M}{2} \ln \frac{1-M}{2} \right] - \mathcal{N} \frac{1}{2} c \epsilon M^2 \quad (457)$$

From this expression it is convenient to derive explicit results for the state equations. In particular $S = -\partial F / \partial T$ and one can recover the result for the heat capacity.

===== [9.4] The Bragg Williams formulation

Consider an Ising model with \mathcal{N} sites, at any dimension, and with any coordination number. Given a spin configuration define

$$\mathcal{N} = \text{total number of spins} \quad (458)$$

$$\tilde{M} = \text{total magnetization} \quad (459)$$

$$M = \tilde{M} / \mathcal{N} \quad (460)$$

$$N_+ = \text{number of up spins} = \frac{1}{2}(\mathcal{N} + \tilde{M}) = \frac{1}{2}\mathcal{N}(1 + M) \quad (461)$$

$$N_- = \text{number of down spins} = \frac{1}{2}(\mathcal{N} - \tilde{M}) = \frac{1}{2}\mathcal{N}(1 - M) \quad (462)$$

$$N_{+-} = \text{number of bonds connecting spins with opposite direction} \quad (463)$$

It follows that

$$\sum \sigma_i = \tilde{M} \quad (464)$$

$$\sum_{\langle ij \rangle} \sigma_i \sigma_j = \frac{1}{2} c \mathcal{N} - 2N_{+-} \quad (465)$$

If we look on two connected spins, there is a probability (N_+ / \mathcal{N}) to have the first up, and a probability (N_- / \mathcal{N}) to have the the second down. The total number of connected spins is $c\mathcal{N}/2$. The Bragg Williams approximation is

$$N_{+-} \approx \frac{1}{2} c \mathcal{N} \times \left[\left(\frac{N_+}{\mathcal{N}} \right) \left(\frac{N_-}{\mathcal{N}} \right) + \left(\frac{N_-}{\mathcal{N}} \right) \left(\frac{N_+}{\mathcal{N}} \right) \right] \quad (466)$$

Assuming that it holds for typical configurations we approximate the energy functional as

$$E[\sigma] \approx -\mathcal{N} \times \left(\frac{1}{2} c \epsilon M^2 + h M \right) \quad (467)$$

We note that this expression with $c = \mathcal{N}$ is formally exact for a fully connected cluster of spins. The number of configuration with magnetization M is

$$g_M = \frac{\mathcal{N}!}{(N_+)! (N_-)!} \approx \text{const} \exp \left[-\mathcal{N} \left(\frac{1}{2} M^2 + \frac{1}{12} M^4 + \dots \right) \right] \quad (468)$$

In order to derive the latter approximation note that the derivative of $\ln(g_M)$ is of the form

$$\frac{1}{2} (\ln(1+x) - \ln(1-x)) \approx x + \frac{1}{3} x^3 + \frac{1}{5} x^5 + \dots \quad (469)$$

With this approximation we get

$$Z = \sum_M \sum_{\sigma \in M} e^{-\beta E[\sigma]} \approx \sum_M g_M e^{-\beta E(M)} = \sum_M e^{-A(M)} \quad (470)$$

$$A(M) = \mathcal{N} \times \left[\frac{1}{2} (1 - \beta c \varepsilon) M^2 + \frac{1}{12} M^4 - \beta h M \right] \quad (471)$$

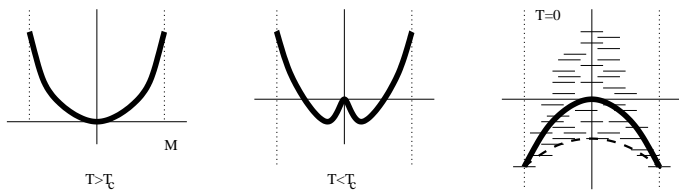
This sum can be evaluated via Gaussian integration. The dominant contribution comes from the M for which $A(M)$ is minimal. One can easily verify that $A'(M) = 0$ coincides with the heuristic mean field equation that has been discussed in a previous lecture. The critical temperature is $T_c = c\varepsilon$. For $T < T_c$ the trivial mean field solution $M = 0$ bifurcates into two stable minima. Symmetry breaking is implied because the limits $h \rightarrow +0$ and $h \rightarrow -0$ do not lead to the same minimum.

===== [9.5] The importance of fluctuations

One can ask whether it is allowed to ignore the quadratic term in $A(M)$. This should be checked self consistently. Using the standard notation $t = (T - T_c)/T_c$, and assuming $t > 0$ we get that the dispersion of M in the Gaussian approximation is $(\mathcal{N}t)^{-1/2}$. The quadratic term is negligible if $|M|^4 \ll t|M|^2$ leading to the condition $|t| \gg 1/\mathcal{N}^{1/2}$. This condition is always satisfied in the thermodynamic limit. The same condition also guarantees that for $t < 0$ the dispersion is much smaller compared with the non-zero mean field $\bar{M} \approx t^{1/2}$.

However, the above analysis is misleading. The Bragg Williams approximation underestimates the effect of fluctuations. We already know from the exact solution of the Ising model that in 1D there is no phase transition at finite temperature. We would like to explain in detail why the fluctuations in 1D smear away the phase transition. Later we shall see that also for $d = 2, 3$ the fluctuations are important: they do not smear away the phase transition, but they modify the state equations in the critical region, which explains the failure of mean field theory there, and the observed *anomalous* values of the scaling exponents.

The problem with the Bragg Williams approximation is implied by the figure below. In the $T = 0$ panel the energy of the states is indicated by bars. By taking the "typical" value of the energy (thick solid line) we ignore a dominant fraction of less typical states that have a very low energy. These states correspond to configurations where the spins are bunched in "zones". The simplest arrangement in 1D has two zones and its energy is $E_b = E_0 + 2\epsilon$, where $E_0 = -\mathcal{N}\epsilon$ is the ground state energy. Consequently the effective barrier between the "all up" and "all down" states is very low (thick dashed line), and the symmetry breaking is avoided at any finite temperature. The formal argument is outlined below. In contrast to that, in 2D the effective barrier is $E_b = E_0 + \mathcal{N}^{1/2}\epsilon$ and therefore symmetry breaking is realized in the thermodynamic limit.



Domain walls.— It is possible to argue that in 1D there is no phase transition at finite temperature. The argument goes as follows: consider a mixture of states with one domain wall. For such state $E[\rho] = E_0 + 2\epsilon$, where ϵ is the cost of the domain wall. But the entropic contribution is $S[\rho] = \ln[\mathcal{N}]$ where \mathcal{N} is the length of the chain. It follows that for any finite T the ground state does not minimize $F[\rho]$ at the thermodynamic limit. Therefore spontaneous magnetization at finite temperature is impossible.

The above argument fails in 2D because the energy of a domain is $E[\rho] = E_0 + \mathcal{N}^{1/2}\epsilon$, which does not threaten the stability of the ground state. In fact it is possible to refine the Domain wall approach and deduce that for the $d = 2$ Ising model there exist spontaneous magnetization at finite temperature [see Huang p.349], in consistency with the exact solution.

The possibility to witness phase transition at $d = 2$ is limited to systems with discrete symmetries. The Mermin-Wagner theorem states that a continuous symmetry cannot be spontaneously broken at finite temperature in $d \leq 2$ systems with short-range interactions. See discussion of the Heisenberg model.

[10] Phase transitions - field theory

===== [10.1] The Landau-Ginzburg model

We would like to take into account the spatial fluctuations of the magnetization $\varphi(x)$ in the calculation of the partition function. Inspired by the Bragg-Williams approach we introduce the following field theory model:

$$Z[h, \text{parameters}; \Lambda, L] = \sum_{\varphi(\cdot)} e^{-A[\varphi(\cdot)]} = \int D\varphi e^{-A[\varphi(\cdot)]} \quad (472)$$

where the sum over configurations becomes an integral with the measure

$$D\varphi = \prod_{x \in L^d} d\varphi_x = \prod_{|k| < \Lambda} d\tilde{\varphi}_k, \quad \tilde{\varphi}_k \equiv \frac{1}{L^d} \int \varphi(x) e^{-ikx} dx \quad (473)$$

In this definition $\tilde{\varphi}_k$ are the Fourier components of $\varphi(x)$, and we are sloppy about an uninteresting overall prefactor. It is implicit that one assumes a finite volume L^d , and a finite momentum cutoff Λ , otherwise the integral is ill defined. To have a momentum cutoff is like to assume that space is discretized with lattice spacing $2\pi/\Lambda$. Accordingly the number of freedoms of the model is $\mathcal{N} = (L\Lambda/2\pi)^d$. The assumed action is

$$A[\varphi(\cdot)] = \int d\mathbf{x} \left(\frac{1}{2} (\nabla\varphi)^2 + \frac{1}{2} r\varphi^2 + \frac{1}{4} u\varphi^4 - h\varphi \right) = L^d \sum_k \left(\frac{1}{2} (k^2 + r) |\tilde{\varphi}(k)|^2 + \dots \right) \quad (474)$$

Note that the summation over the k components of the field is conventionally written as an integral with the measure $[L/(2\pi)]^d dk$. The convention with regard to the prefactor of the first term fixes the dimensions of φ , and hence of the other model parameters. We write these dimensions as L^d , accordingly

$$d_\varphi = -\frac{d-2}{2}, \quad d_h = -\frac{d+2}{2}, \quad d_r = -2, \quad d_u = -(4-d), \quad (475)$$

The model has a thermodynamic limit, hence L is not significant, and we can calculate the Helmholtz free energy F per unit length. In contrast to that Λ is significant, and accordingly we realize that the model contains *two* significant dimensionless parameters $\tilde{r} = r/\Lambda^2$ and $\tilde{u} = u/\Lambda^{4-d}$. Relating to the Bragg-Williams approximation we identify $r \propto (T - T_c^{(0)})/T$, where $T_c^{(0)}$ is the mean field critical temperature. In fact we shall see that the field theory analysis implies that the actual critical temperature is pushed down due to the fluctuations ($r_c < 0$). In the 1D case the critical temperature is pushed to zero ($r_c = -\infty$).

The Landau-Ginzburg model stands by itself as a prototype model. Note however that there is also a possibility to motivate it by direct reduction from the Ising model. For this purpose one replaces the discrete summation over $\sigma = \pm 1$ by an integration over φ with a weight function:

$$\sum_{\sigma(\cdot)} \rightarrow \int \prod_x d\varphi_x e^{-\frac{1}{4}u(\varphi_x^2 - 1)^2} \quad (476)$$

One should realize that the ferromagnetic interaction $-\sigma(x)\sigma(x')$ corresponds to differences $(\varphi(x) - \varphi(x'))^2$, and hence translates to the gradient term in the Landau-Ginzburg model.

The field theory that corresponds to the Ising model contains a real field. It reflects the discrete mirror (up/down) symmetry of the system. More generally we can consider a system that has a continuous rotational symmetry. In such case $\varphi = (\varphi_1, \varphi_2, \varphi_3)$ is a vector and the Action should be modified in an obvious way. Of particular interest is to have complex field $\varphi = (\varphi_1, \varphi_2)$ that describes a system with continuous gauge symmetry: this can be regarded as a rotational symmetry in two dimensions.

===== [10.2] Digression - Gaussian integrals

The partition function can be calculated exactly whenever the action is a quadratic form. The so-called Gaussian integral reduces to the product of \mathcal{N} one dimensional integrals if we transform it to a basis in which the quadratic form is diagonal. For a system that has translation symmetry it is momentum space.

$$\int D\varphi e^{-\frac{1}{2} \sum_{i,j} A_{ij} \varphi_i \varphi_j + \sum_i h_i \varphi_i} = \prod_k \int d\tilde{\varphi}_k e^{-\frac{1}{2} a_k \tilde{\varphi}_k^2 + \tilde{h}_k \varphi_i} \quad (477)$$

$$= \prod_k \left(\frac{2\pi}{a_k} \right)^{1/2} e^{\frac{1}{2} \left(\frac{1}{a_k} \right) h_k^2} = \sqrt{\det(2\pi G)} \exp \left[\frac{1}{2} \sum_{i,j} G_{ij} h_i h_j \right] \quad (478)$$

here $G = A^{-1}$, and note that $\det(G) = 1/\det(A)$. Note also that going back to the original basis, in the case of position-to-momentum transformation implies that $G(r)$ is the Fourier transform of $1/a(k)$.

From the above result, it follows that $G(r)$ is the correlation function $\langle \varphi(r) \varphi(0) \rangle$ for $h = 0$. Otherwise $\langle \varphi \rangle$ is non-zero, and it equals to field $\bar{\varphi}$ that minimizes that action. It satisfies the equation $A\varphi = h$, whose solution is $\bar{\varphi} = Gh$. Hence G can be regarded as the "Green function".

===== [10.3] The mean field approximation

We define the mean field $\bar{\varphi}$ via the equation $A(\varphi) = \text{minimum}$. The mean field for an homogeneous field $h(x) = h$ is obtained from the equation $r\varphi + u\varphi^3 = h$. In particular for $h = \pm 0$ we get

$$\bar{\varphi}_0 = \begin{cases} 0, & \text{for } r > 0 \\ \pm \left(\frac{-r}{u} \right)^{\frac{1}{2}}, & \text{for } r < 0 \end{cases} \quad A[\bar{\varphi}_0] = \begin{cases} 0, & \text{for } r > 0 \\ - \left(\frac{3r^2}{4u} \right)^{\frac{1}{2}}, & \text{for } r < 0 \end{cases} \quad (479)$$

More generally the mean field equation is

$$(-\nabla^2 + r) \varphi + u\varphi^3 = h(x) \quad (480)$$

The solution up to first order in $h(x)$ is

$$\bar{\varphi}(x) = \bar{\varphi}_0 + \int g(x-x') h(x') dx' + \mathcal{O}(h^2) \quad (481)$$

where

$$g(x-x') = \int \frac{dq}{(2\pi)^d} \frac{e^{iq(x-x')}}{q^2 + (1/\xi)^2} \quad \xi = \begin{cases} r^{-\frac{1}{2}}, & \text{for } r > 0 \\ (-2r)^{-\frac{1}{2}}, & \text{for } r < 0 \end{cases} \quad (482)$$

We recall that $g(r)$ is both the Green function and the correlation function in the Gaussian approximation. Hence the mean field exponents are $\nu = 1/2$ and $\eta = 0$.

===== [10.4] The Gaussian approximation

We assume $r > 0$, so the action has a single minimum at $\bar{\varphi}$. Let us neglect the quartic term. Then the partition sum factorizes in k space. Not caring about global prefactor we get:

$$Z = e^{-A[\bar{\varphi}]} \prod_k \int d\tilde{\varphi}_k \exp \left[-\frac{L^d}{2} (k^2 + (1/\xi)^2) \tilde{\varphi}_k^2 \right] = e^{-A[\bar{\varphi}]} \prod_k \left(\frac{1}{k^2 + (1/\xi)^2} \right)^{1/2} \quad (483)$$

For $r < 0$ we have to add the contributions that come from two minima, but if $h > 0$ the dominant contribution will come from the vicinity of the $\bar{\varphi} > 0$ minimum. Assuming that the result is dominated by a single minimum, either above or below the critical temperature, the free energy is

$$F(T) = TA[\bar{\varphi}] + \frac{T}{2} \sum_k \ln(k^2 + (1/\xi)^2) \quad (484)$$

In particular we can derive from this expression the Gaussian prediction for the heat capacity. The "mean field" term, that originates from $A[\bar{\varphi}]$, contributes a discontinuity. The singular contribution at the vicinity of T_c comes from the second term, and originates from the second derivative with respect to r . Accordingly

$$C(T) = -T \frac{d^2 F}{dT^2} \sim \int_0^\Lambda \frac{k^{d-1} dk}{(k^2 + r)^2} \sim |T - T_c|^{-(4-d)/2}, \quad \text{for } d < 4 \quad (485)$$

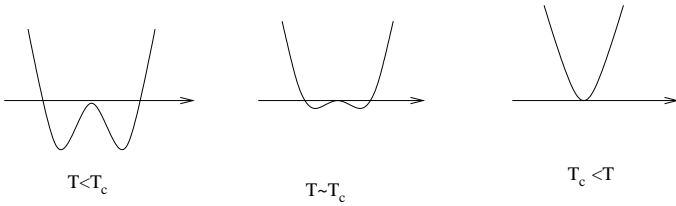
Hence the modified mean field exponent $\alpha = [2 - (d/2)]$.

===== [10.5] Symmetry breaking

Let us first assume that $r > 0$ and ask whether we can trust the Gaussian approximation. Higher non-Gaussian terms in the expansion of $A[\varphi]$ around $\bar{\varphi}$ were neglected in the above treatment. The condition for this neglect is found in the same way as in the Bragg-Williams analysis. Namely, the neglect of the non-Gaussian term is justified if $u\varphi^4 \ll r\varphi^2$, where $\varphi^2 \sim 1/\xi^{d-2}$ is estimated from Ornstein-Zernike. This leads to the Ginzburg Criterion

$$|T - T_c^{(0)}| \gg \text{const } u^{2/(4-d)} \quad (486)$$

This condition defines the border of the critical region. Within the critical region the Gaussian approximation breaks down because of non-Gaussian fluctuations.



We now turn to the question whether the fluctuations modify T_c or endanger the possibility of having a phase transition. Let us take a closer look at the fluctuations. Within the framework of the Gaussian approximation the variance of each Fourier component is

$$\text{Var}(\varphi_k) = \frac{1}{L^d} \left(\frac{1}{k^2 + (1/\xi)^2} \right) \quad (487)$$

The field amplitude $\varphi(x)$ at a given point in space is the sum of \mathcal{N} independent Fourier components. Accordingly the total variance is

$$\text{Var}(\varphi(x)) = \sum_k \text{Var}(\varphi_k) = \int_{1/L}^{1/\Lambda} \frac{dk}{(2\pi)^d} \frac{1}{k^2 + (1/\xi)^2} = g(0) \quad (488)$$

This integral is dominated by the low frequency modes if $d < 4$. The Bragg-Williams analysis keeps only the $k = 0$ fluctuations, leading to the diminishing result ξ^2/L^d , while the Gaussian analysis takes all the $(L/\xi)^d$ effective modes into account, leading to a non-diminishing result $1/\xi^{d-2}$.

We see that $\text{Var}(\varphi)$ diverge as T approach $T_c^{(0)}$ from above. Let us assume that for $T \ll T_c^{(0)}$ there is a symmetry breaking, such that $\langle \varphi \rangle$ jumps from $+\bar{\varphi}$ to $-\bar{\varphi}$ as h is varied across $h = 0$. Obviously, in order to observe a phase transition we have to require

$$\sqrt{\text{Var}(\varphi)} \ll \bar{\varphi} \quad (489)$$

It is not difficult to show that within the Gaussian approximation this self-consistency requirement leads again to the Ginzburg Criterion. However, this does not imply that there is actually a phase transition. We shall discuss below two cases in which fluctuations completely destroy the possibility to observe a phase transition.

First we refer to the case where the order parameter has a continuous rather than a discrete symmetry. To be specific let us assume a complex order parameter $\varphi = (\varphi_1, \varphi_2)$. In such case the potential $V(\varphi) = (1/2)r\varphi^2 + (1/4)\varphi^4$ looks like a Mexican hat for $r < 0$. It means that instead of having two minima we have a continuous set of minima. This implies that the low frequency excitations of the system are phonon-like, called magnons in the ferromagnetic context. In general the excitations that appear if a continuous symmetry is broken are known as Goldstone excitations. They have some dispersion $\omega = c|k|$. Coming back to the partition sum, we see that we have to include the Goldstone excitations in the $\text{Var}(\varphi)$ calculation, leading formally to an integral over $1/k^2$ instead of $1/(k^2 + (1/\xi)^2)$. The integral is "infrared divergent" unless $d > 2$. We conclude that the fluctuations destroy the possibility to observe a phase transition at $d = 2$. This is known as the Mermin-Wagner theorem.

Going back to the real field case, there are no Goldstone excitations, but we know from the analysis of the Ising model that fluctuations destroy the possibility to observe a phase transition if $d = 1$. This should be contrasted with $d > 1$, for which the critical point is shifted down ($r_c < 0$) but remains finite (see discussion of the RG analysis). The reason for the lack of phase transition here is more subtle. It is clear, even if we have a phase transition, that $\text{Var}(\varphi) \sim \bar{\varphi}^2$ on the critical line. The question is whether it becomes $\text{Var}(\varphi) \ll \bar{\varphi}^2$ for any finite h away from the critical line. This depends on the height of the "barrier" between the two minima, and therefore cannot be deduced from the Ginzburg criterion: the latter is based on a local Gaussian approximation that does not know anything about the height of the "barrier". We shall see in the next section that in the $d = 1$ case the crossover has a finite width: there is no abrupt change in $\langle \varphi \rangle$ as $h = 0$ is crossed.

===== [10.6] The one dimensional model

The one-dimensional field model can be solved exactly. This is merely a variation on the "transfer matrix" method. The $D\varphi$ integral is sliced and written as a trace over the product of \mathcal{N} matrices. Each matrix can be written as $\exp(-dxH)$ where H is the "Hamiltonian". One realize that this is nothing else but the Feynman path integral in "imaginary time". Let us define

$$H = -\frac{1}{2}\frac{\partial^2}{\partial\varphi^2} + V(\varphi) = -\frac{1}{2}\frac{\partial^2}{\partial\varphi^2} + \left[\frac{1}{2}r\varphi^2 + \frac{1}{4}\varphi^4\right] \quad (490)$$

using the notation $\dot{\varphi} = d\varphi/dx$ and $x = \tau$ with periodic boundary conditions over $[0, L]$, the calculation of the partition function goes as follow:

$$Z = \int D\varphi e^{-\int_0^L \frac{1}{2}\dot{\varphi}^2 + V(\varphi)d\tau} = \text{trace}(e^{-LH}) = \sum_n e^{-L\mu_n} \quad (491)$$

where μ_n are the eigenvalues of H . In the thermodynamic limit $F(T, h) = LT\mu_0$ where μ_0 is the ground state energy of H . Similarly $\langle \varphi \rangle$ is just the ground state expectation value. For the correlation function we get

$$g(r) \propto \text{trace} \left[e^{-(L-r)H} \varphi e^{-rH} \varphi \right] \propto \sum_n |\langle n | \varphi | 0 \rangle|^2 e^{-r(\mu_n - \mu_0)} \quad (492)$$

where in the last equality we already dropped the terms that vanish in the thermodynamic limit. We see that the long tails are characterized the correlation length $\xi = 1/(\mu_1 - \mu_0)$. This correlation length does not diverge, reflecting that the variation of $\langle \varphi \rangle$ is smooth. The crossover at $h = 0$ has a width that equals the tunnel splitting $(\mu_1 - \mu_0)$.

The above analysis demonstrates that quite generally quantum analysis of the ground state in d dimensions is like classical field theory at finite temperature in $d_{cl} = d + 1$ dimensions. This implies that we can hope to observe "quantum phase transitions" at $d > 1$, notably at $d = 2$, because it corresponds to symmetry breaking of a continuous order parameter at $d_{cl} > 2$.

===== [10.7] The Heisenberg model

The Heisenberg model relates to a three component vector field \mathbf{S} . It is described by the Hamiltonian

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \quad (493)$$

The field theory version of the Heisenberg model is the nonlinear sigma model (NLSM), where $S(x)$ is a vector field that obeys the constraint $|S(x)| = 1$. The NLSM energy functional is commonly written as

$$E[S] = \frac{1}{2g} \int |\nabla S|^2 dx \quad (494)$$

The Mermin-Wagner theorem:— In the Heisenberg model the order parameter has a continuous symmetry with respect to spin rotations. This is different from the Ising model where the symmetry is discrete (up/down). The Mermin-Wagner theorem states that continuous symmetries cannot be spontaneously broken at finite temperature in $d \leq 2$ systems with short-range interactions. This is due to long-range fluctuations, corresponding to massless "Goldstone modes". These fluctuations cost little energy, while contribute large entropy. Hence at finite temperatures the $T = 0$ broken symmetry is washed away.

Let us outline the argument that explains the dimensionality issue. Assume that there is a long range order. Use the Gaussian approximation to calculate the correlation function around the selected minimum. The Goldstone modes are massless (which is like $r = 0$ in the Landau-Ginzburg model). Hence $g(r) = \text{FT}[1/k^2]$. The area under $g(r)$ diverges due to the low wavelength fluctuations if $d \leq 2$, indicating that the minimum is washed away.

===== [10.8] The XY model

The XY model relates to a two component vector field \mathbf{S} . It can be regarded as a 2D version of the Heisenberg model. The orientation of the i th spin in the XY plane is φ_i . Accordingly we can write

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \cos(\varphi_i - \varphi_j) \quad (495)$$

Its the continuous field version is defined by the energy functional

$$E[\varphi] = \frac{K}{2\pi} \int (\nabla \varphi)^2 dx \quad (496)$$

The low lying excitations of this model are vortices. For example, a single vortex at the origin is represented by

$$\varphi(z) = q \arg(x, y) = q \tan^{-1}(y/x) \quad (497)$$

$$|\nabla \varphi| = (q/r) \text{ [tangential]} \quad (498)$$

$$E[\varphi] = Kq \ln(L/a) \quad (499)$$

where L is the radius of the system, and a is the lattice spacing. One realizes that $\vec{F} = \nabla \varphi$ is like a 90deg rotated version of a field due to a charge q in a 2D electrostatic problem, while $E[\varphi]$ corresponds to the electrostatic energy.

Accordingly if we have several vortexes we get

$$E[\varphi] = \text{const} - K \sum_{\langle i,j \rangle} q_i q_j \ln |r_i - r_j| \quad (500)$$

which is formally the expression for the energy of a Coulumb gas in 2D.

Note about complex representation.— Consider a field $\vec{F} = (F_x, F_y)$ in 2D that has no sources ($\nabla \cdot \vec{F} = 0$) and no circulations ($\nabla \times \vec{F} = 0$). These two conditions are the Cauchy-Riemann equations that allow to represent the field by a complex differentiable function $f(z) = F_x - iF_y$, where $z = x + iy$. Note that in sloppy notations $\vec{F} = f(z)^*$. Note that such functions are called holomorphic and hence they are analytic, i.e. have a convergent Taylor expansion at any point. Note also that a holomorphic function can be regarded as a conformal map $w = f(z)$ that induces a local transformation $df = Cdz$, where the local derivative C can be regarded as a rotation (due to its phase) combined with dilation (due to its modulo). From the Cauchy-Riemann no-circulation condition it follows that the field can be derived from a scalar potential ($\vec{F} = -\nabla V$). Optionally from the Cauchy-Riemann no source condition it follows that the field can be derived from a vector potential ($\vec{F} = \nabla \times (0, 0, A)$). We can summarize these two options by defining a complex potential $\Psi(z) = V(z) + iA(z)$ such that $f(z) = -\Psi'(z)$. The lines of constant $A(z)$ are called "stream lines", while the lines of constant $V(z)$ are called "propagation fronts". Differences of A have the meaning of "flux", while differences of V have the meaning of "work". For a point charge in a 2D electrostatic problem the Coulomb field is $f(z) = q/z$ and $\Psi(z) = -q \ln(z)$ corresponding to $V(x, y) = -q \ln(r)$. The vortex in the XY model is just a rotated version of a Coulomb field with $f(z) = -iq/z$ and $\Psi(z) = -iq \ln(z)$. The energy functional can be written as

$$E[\Psi] = \frac{K}{2\pi} \int |\Psi'(z)|^2 dx \quad (501)$$

The Kosterlitz-Thouless transition.— Let us see what happens if we have a collection of vortexes. The entropy which is associated with the number of possibility to position the vortex in the lattice is $S = \ln[(L/a)^2]$. Accordingly the introduction of a vortex into the system implies

$$F[\rho] = E[\rho] - TS[\rho] = (K - 2T) \ln[(L/a)] \quad (502)$$

Hence for $T > (K/2)$ the creation of a vortex is favored, so we expect to have a gas of quasi-independent vortexes. For $T < (K/2)$ these vortexes have to pair, which is like not having vortexes. The above argumentation implies an "infinite order phase transition". In consistency with the Mermin-Wagner theorem it does not lead to "long range order". Rather it describes a transition from "conventional disordered phase" at high temperature, to "quasi-long-range ordered phase" at low-temperature. The correlation function goes from exponential above the critical temperature, to powerlaw at the critical temperature and below. At the critical temperature $g(r) = 1/r^{1/4}$.

===== [10.9] Renormalization Group (RG) analysis

In the field theory model, we should perform the sum over all the field configurations $\varphi(x)$ or equivalently over all of the Fourier components $\tilde{\varphi}_k$. In order to get a finite result we should in general use two cutoff parameters:

$$L = \text{linear size of the model} \quad (503)$$

$$\Lambda = \text{largest momentum scale} \quad (504)$$

Consequently we define

$$F(a, r, u, h, c; \Lambda, L) = -\ln Z \quad (505)$$

where the action of the Landau-Ginzburg model is

$$A[\varphi; a, r, u, h, c] = \int d\mathbf{x} \left(\frac{1}{2} a (\nabla \varphi)^2 + \frac{1}{2} r \varphi^2 + \frac{1}{4} u \varphi^4 - h \varphi + c \right) \quad (506)$$

where by convention the field φ is scaled such that $a = 1$. Note that re-scaling of φ shifts the constant c , which we ignore below, because it does not affect the correlation function. Below we use the symbolic notation g for any of the parameters $\{r, u, h\}$ that define the model.

Engineering scaling.— There is always a trivial “engineering” scaling relation

$$F(s^{d_g}g, a; \Lambda/s, sL) = F(g, a; \Lambda, L) \quad (507)$$

The dimensions d_r and d_u and d_h are fixed by the requirement $d_a = 0$. When combined with the thermodynamic limit we get $F(s^{d_g}g, a; \Lambda/s, L) = s^{-d}F(g, a; \Lambda, L)$, which we prefer to rewrite as follows:

$$F(g, a; \Lambda/s) = s^{-d}F(s^{-d_g}g, a; \Lambda) \quad (508)$$

From now on we suppress L , and assume that the volume of the system is fixed.

Step1 of RG.— Perturbation theory allows to integrate the high Fourier components within a shell $\Lambda - \delta\Lambda < k < \Lambda$. This is called “step1” of the RG procedure, leading to

$$F(g, a; \Lambda) = F(g', a'; \Lambda/s) \quad (509)$$

where $s = \Lambda/(\Lambda - \delta\Lambda) = e^{\delta\Lambda/\Lambda}$ is called the scaling parameter. Later it is convenient to use the optional parametrization $s = e^\tau$. The elimination of the high Fourier components spoils both Λ and a .

Step2 of RG.— In “step2” of the RG procedure the original value of Λ is restored using the engineering scaling relation. Accordingly we write

$$F(g, a) = s^{-d} F(s^{-d_g}g', a') \quad (510)$$

where both L and Λ are fixed and hence not indicated.

Step3 of RG.— In “step3” of the RG procedure the field φ is re-scaled, such that the convention $a = 1$ is restored, hence one can write

$$F(g) = s^{-d} F(g_s) \quad (511)$$

where now we suppress a as well, because it is fixed. In the case of the Landau-Ginzburg model we can illustrate the RG flow in a (r, u, τ) space. Increasing τ means lower resolution description of the systems, with effective coupling g_s where $s = e^\tau$. From the perturbation theory analysis one finds a relation $g_s = R(s)g$ that maps points g to points g_s . We have the group property $R(s_2)R(s_1) = R(s_2s_1)$, or optionally we can write $R(\tau_2)R(\tau_1) = R(\tau_2 + \tau_1)$.

RG equation.— It is convenient to re-define each parameter as dimensionless using the substitution $g := \Lambda^{d_g}g$. Consequently one obtains an equation of the type

$$\frac{dg}{d\tau} = \beta(g), \quad [\text{optional notation: } d\tau = d \ln \Lambda] \quad (512)$$

Note that in the right hand side Λ is absorbed due to the re-definition of the units. In the Landau-Ginzburg model case the RG equation is

$$\frac{d\tilde{r}}{d\tau} = 2\tilde{r} - 3\tilde{r}\tilde{u} + 3\tilde{u} \quad (513)$$

$$\frac{d\tilde{u}}{d\tau} = (4 - d)\tilde{u} - 9\tilde{u}^2 \quad (514)$$

where $\tilde{r} = r/\Lambda^2$ and $\tilde{u} = u/\Lambda^{4-d}$. Note that u of Huang is what we defined as $u/4$.

RG flow.— The RG equation defines flow in g space. We want to understand how the RG flow explains the observed universal critical behavior. Consequently we identify the "critical point" as the fixed point of the RG flow. In the Landau-Ginzburg model we have two fixed points: The Gaussian fixed point $\tilde{r}_0 = 0$, $\tilde{u}_0 = 0$ and the nontrivial fixed point $\tilde{r}_c = -(4-d)/6$, $\tilde{u}_c = (4-d)/9$. For $d < 4$, as expected from the Ginzburg criterion, the Gaussian fixed point is unstable and the flow is dominated by the nontrivial fixed point. One observes that the critical temperature (r_c) is shifted below the mean field Gaussian value.

The critical exponents.— We want to understand how the RG flow explains the scaling hypothesis. In the vicinity of the fixed point we can linearize the RG equation. After linear transformation and shift, such that $g = 0$ is the fixed point, we get an equation of the type $dg_s/d\tau = \lambda g$, whose solution is $g_s = e^{\lambda\tau} g$. Consequently we deduce that

$$F(g) = s^{-d} F(s^{-D_g} g) \quad (515)$$

where $D_g = -\lambda$ is called the anomalous dimension. Note that the D of Huang is defined with opposite sign (he is using inverse length units). Note again that " g " stands for a collection of parameters, each having its own "dimension". The temperature is considered to be a "relevant" parameter because we can associate with it a negative dimension $D < 0$. This means that the coarse grained system looks less and less critical as τ is increased. Parameters with positive dimension $D > 0$ vanish from the model due to the coarse graining and therefore are called "irrelevant". For further details see Huang.

Fluctuations and Response

[11] Fluctuations

In order to know the expectation value of an operator we need only spectral information which is present in $g(E, X)$ or in $Z(\beta, X)$. Note that these functions contains only spectral information about the system (no information on the dynamics). Still it is enough for the calculation of the conservative force. For example, in case of a canonical preparation

$$\langle \mathcal{F} \rangle_0 = \left\langle -\frac{\partial \mathcal{H}}{\partial X} \right\rangle = \sum_n p_n \left(-\frac{\partial E_n}{\partial X} \right) = \frac{1}{\beta} \frac{\partial \ln(Z)}{\partial X} \quad (516)$$

In contrast to that, the fluctuations of $\mathcal{F}(t) - \langle \mathcal{F} \rangle_0$ require knowledge of the dynamics, and cannot be calculated from the partition function. For simplicity of presentation we assume below that the fluctuating quantity of interest is re-defined such that $\langle \mathcal{F} \rangle_0 = 0$.

===== [11.1] The classical power spectrum

Consider a stationary stochastic classical variable $F(t)$, and define its correlation function as

$$C(t_2 - t_1) = \langle F(t_2)F(t_1) \rangle \quad (517)$$

The power spectrum $\tilde{C}(\omega)$ is the Fourier transform of $C(\tau)$, where $\tau = t_2 - t_1$ is the time difference. In practice a realization of F within time interval $0 < t' < t$ can be Fourier analyzed as follows:

$$F_\omega = \int_0^t F(t') e^{i\omega t'} dt' \quad (518)$$

and we get the "Wiener-Khinchin theorem"

$$\langle |F_\omega|^2 \rangle = \tilde{C}(\omega) \times t \quad (519)$$

where we assume that t is much larger compared with the correlation time.

===== [11.2] The quantum power spectrum

We consider a system whose dynamics is generated by Hamiltonian \mathcal{H} . We assume that it is prepared in a stationary state, possibly but not necessarily a thermal states. Our interest is in the fluctuations of an observable \mathcal{F} . We use the common interaction picture notation $\mathcal{F}(t) = e^{i\mathcal{H}t} \mathcal{F} e^{-i\mathcal{H}t}$. The non-symmetrized correlation function of \mathcal{F} is defined as

$$S(t) = \langle \mathcal{F}(t) \mathcal{F}(0) \rangle \quad (520)$$

This function is complex, but its Fourier transform is real and can be calculated as follows:

$$\tilde{S}(\omega) = \int_{-\infty}^{\infty} S(t) e^{i\omega t} dt = \sum_n p_n \sum_m |\mathcal{F}_{mn}|^2 2\pi \delta \left(\omega - \frac{E_m - E_n}{\hbar} \right) \quad (521)$$

In the case of a *microcanonical* preparation at some energy E , this is the same object that appears in the Fermi-Golden-rule (FGR) for rate of decay due to transitions to other levels, namely

$$\Gamma_{\text{FGR}} = \tilde{S}_E(\Omega) \times A^2, \quad \text{for } \mathcal{H} - f(t)\mathcal{F}, \text{ with } f(t) = Ae^{-i\Omega t} \quad (522)$$

See further discussion of the FGR in the Kubo formula section. In the above formula $\omega > 0$ corresponds to absorption of energy (upward transitions), while $\omega < 0$ corresponds to emission (downward transitions).

It is a straightforward algebra to show that for a *canonical* preparations at temperature T , where $p_n \propto \exp(-E_n/T)$, there is a detailed balance relation:

$$\tilde{S}_T(-\omega) = \exp\left(-\frac{\hbar\omega}{T}\right) \tilde{S}_T(\omega) \quad (523)$$

This implies that if we couple to the system another test system (e.g. a two level “thermometer”) it would be driven by the fluctuations into a canonical state with the same temperature. We define

$$\tilde{C}(\omega) = \frac{1}{2} \left(\tilde{S}(\omega) + \tilde{S}(-\omega) \right) \quad (524)$$

$$\tilde{K}(\omega) = \frac{i}{\hbar} \left(\tilde{S}(\omega) - \tilde{S}(-\omega) \right) \quad (525)$$

and deduce that at thermal equilibrium they are related as follows:

$$\tilde{K}(\omega) = i \frac{2}{\hbar} \tanh\left(\frac{\hbar\omega}{2T}\right) C(\omega) \quad (526)$$

We shall see later that $\tilde{K}(\omega)$ determines the absorption coefficient of the system, hence the above relation is going to be the basis for a “fluctuation-dissipation relation”. But first we would like to generalize the characterization of fluctuations to the case of having several different observables.

===== [11.3] Fluctuations of several observables

Give several observables \mathcal{F}^j , and assuming that the system is prepared in a stationary state, the fluctuations can be characterized by the correlation function

$$S^{kj}(t) = \langle \mathcal{F}^k(t) \mathcal{F}^j(0) \rangle \quad (527)$$

The associated spectral function $\tilde{S}^{kj}(\omega)$ is defined by a Fourier transform. For simplicity we use the notations $\mathcal{F}^1 = A$ and $\mathcal{F}^2 = B$, and write the spectral decomposition

$$\tilde{S}^{AB}(\omega) = \sum_n p_n \sum_{m(\neq n)} A_{nm} B_{mn} 2\pi \delta\left(\omega - \frac{E_m - E_n}{\hbar}\right) \quad (528)$$

It is convenient to write $S^{AB}(t)$ as the sum of two *real* spectral functions that have a good classical limit:

$$S^{AB}(t) = C^{AB}(t) - i \frac{\hbar}{2} K^{AB}(t) \quad (529)$$

$$C^{AB}(t) \equiv \frac{1}{2} \langle A(t) B(0) + B(0) A(t) \rangle \quad (530)$$

$$K^{AB}(t) \equiv \frac{i}{\hbar} \langle [A(t), B(0)] \rangle \quad (531)$$

We use the notations $\tilde{S}^{AB}(\omega)$, and $\tilde{C}^{AB}(\omega)$, and $\tilde{K}^{AB}(\omega)$ for their Fourier transforms. With regard to the spectral decomposition of $\tilde{C}^{AB}(\omega)$ and $\tilde{K}^{AB}(\omega)$ we note that it is convenient to write $p_n = f(E_n)$. We can simplify these

expressions by interchanging the dummy indexes n, m in the second term. Thus we get

$$\tilde{C}^{AB}(\omega) = \frac{1}{2} \sum_{n,m} (f(E_n) + f(E_m)) A_{nm} B_{mn} 2\pi\delta\left(\omega - \frac{E_m - E_n}{\hbar}\right) \quad (532)$$

$$\tilde{K}^{AB}(\omega) = i\omega \sum_{n,m} \frac{f(E_n) - f(E_m)}{E_m - E_n} A_{nm} B_{mn} 2\pi\delta\left(\omega - \frac{E_m - E_n}{\hbar}\right) \quad (533)$$

Note that for a canonical state $f(E_n) - f(E_m) = \tanh((E_n - E_m)/(2T)) \times (f(E_n) + f(E_m))$. Note also that in the expression for $\tilde{K}^{AB}(\omega)$, the ω cancels the $E_m - E_n$ denominator. The reason for pulling ω out of the sum is to emphasize the low frequency dependence.

===== [11.4] Reciprocity relations

There are some reciprocity relations that should be noticed. First we note that by definition $S^{AB}(t) = [S^{BA}(-t)]^*$. In practice it is more illuminating to write the FTed version of this reciprocity relation, which can be directly deduced by inspection of the spectral decomposition. Namely,

$$\tilde{S}^{AB}(\omega) = [\tilde{S}^{BA}(\omega)]^* \quad (534)$$

It follows that $\tilde{C}^{AB}(\omega) = [\tilde{C}^{BA}(\omega)]^*$, while $\tilde{K}^{AB}(\omega) = -[\tilde{K}^{BA}(\omega)]^*$. There is a second reciprocity relation that follows from time reversal invariance. Also here it is simpler to look on the spectral decomposition and to remember that $[A_{n,m}]^* = A_{n^*,m^*}$, where n^* and m^* are the eigenstates of the time reversed Hamiltonian. In practical terms it means that one has to reverse the sign of the magnetic field h . Consequently $[\tilde{S}^{BA}(\omega; h)]^* = [\pm]\tilde{S}^{BA}(\omega; -h)$, where the plus (minus) applies if the signs of A and B transform (not) in the same way under time reversal. Combining with the trivial reciprocity relation we get the Onsager reciprocity relation

$$\tilde{S}^{AB}(\omega; h) = [\pm]\tilde{S}^{BA}(\omega; -h) \quad (535)$$

The Kubo formula that we discuss in the next section implies that the same reciprocity relations hold for the response kernel α^{kj} , to the susceptibility χ^{kj} and to the DC conductance \mathbf{G}^{kj} . These are called Onsager reciprocity relations

===== [11.5] Detailed balance

We can also generalize what we called "detailed balance relation". In the quantum context this is a relation between "positive" and "negative" frequencies. Assuming that the system is prepared in a canonical state we have

$$\tilde{S}_T^{AB}(-\omega) = \exp\left(-\frac{\hbar\omega}{T}\right) \tilde{S}_T^{BA}(\omega) \quad (536)$$

From here it follows that

$$\tilde{K}_T^{AB}(\omega) = i\frac{2}{\hbar} \tanh\left(\frac{\hbar\omega}{2T}\right) \tilde{C}_T^{AB}(\omega) \quad [\text{quantum canonical version}] \quad (537)$$

The Kubo formula that we discuss in the next section is expressed using $\tilde{K}^{AB}(t)$. But it is more convenient to use $\tilde{C}^{AB}(t)$. The above relation between the two is the basis for the FD relation and its generalizations.

It is interesting to look on the classical limit of the generalized detailed balance relation, which can be obtained by averaging of the classical microcanonical version (a clue with regard to the derivation of the latter will be presented

later when we discuss the classical fluctuation-dissipation relation):

$$\tilde{K}_T^{AB}(\omega) = i\omega \times \frac{1}{T} \tilde{C}_T^{AB}(\omega) \quad [\text{classical canonical version}] \quad (538)$$

$$\tilde{K}_E^{AB}(\omega) = i\omega \times \frac{1}{g(E)} \frac{d}{dE} [g(E) \tilde{C}_E^{AB}(\omega)] \quad [\text{classical microcanonical version}] \quad (539)$$

Optionally the classical canonical version can be regarded as the low frequency limit of the quantum relation. It looks very nice in time domain. Omitting the superscript and using dot for time derivative it reads

$$K_T(t) = -\frac{1}{T} \dot{C}_T(t) \quad (540)$$

We shall use the latter version in order to derive a generalized fluctuation-dissipation relation for the DC conductance.

[12] Linear response theory

===== [12.1] The notion of linear response

Let us assume that $X(t)$ is an input signal, while $F(t)$ is the output signal of some black box. Linear response means that the two are related by

$$F(t) = \int_{-\infty}^{\infty} \alpha(t-t') X(t') dt' \quad (541)$$

The response kernel $\alpha(t-t_0)$ can be interpreted as the output signal that follows a $\delta(t-t_0)$ input signal. We assume a causal relationship, meaning that $\alpha(\tau) = 0$ for $\tau < 0$. The linear relation above can be written in terms of Fourier components as:

$$F_{\omega} = \chi(\omega) X_{\omega} \quad (542)$$

where $\chi(\omega)$ is called the generalized susceptibility. Because of causality $\chi(\omega)$ is analytic in the upper complex plane. Consequently its real and imaginary parts are inter-related by the Hilbert transform:

$$\text{Re}[\chi(\omega)] = \int_{-\infty}^{\infty} \frac{\text{Im}[\chi(\omega')]}{\omega' - \omega} \frac{d\omega'}{\pi} \quad (543)$$

(the reverse Hilbert transform goes with an opposite sign). The imaginary part of $\chi(\omega)$ is the sine transforms of $\alpha(\tau)$, and therefore it is proportional to ω for small frequencies. Consequently it is useful to define

$$\chi_0(\omega) \equiv \text{Re}[\chi(\omega)] = \int_0^{\infty} \alpha(\tau) \cos(\omega\tau) d\tau \quad (544)$$

$$\eta(\omega) \equiv \frac{\text{Im}[\chi(\omega)]}{\omega} = \int_0^{\infty} \alpha(\tau) \frac{\sin(\omega\tau)}{\omega} d\tau \quad (545)$$

and write

$$F_{\omega} = \chi_0(\omega) X_{\omega} - \eta(\omega) \dot{X}_{\omega} \quad (546)$$

For low frequency "DC driving" we can regard χ_0 and η as constants. Note that

$$\eta \text{ [DC limit]} = \int_0^{\infty} \alpha(\tau) \tau d\tau \quad (547)$$

===== [12.2] Rate of energy absorption

We first consider the case of one parameter driving, where \mathcal{F} is the generalized force conjugate to X . The postulated LRT relation regards $X(t)$ as a small deviation from some reference value $X_0 = 0$, while $F(t)$ is the induced deviation from the equilibrium value. Accordingly $F_{\omega} = \chi_0 X_{\omega} - \eta \dot{X}_{\omega}$ implies

$$\langle \mathcal{F} \rangle_t = \langle \mathcal{F} \rangle_0 + \chi_0 (X - X_0) - \eta \dot{X} = \langle \mathcal{F} \rangle_X - \eta \dot{X} \quad (548)$$

The in-phase response gives the conservative effect, and in the second equality it has been absorbed into the first term. The out-of-phase response gives the dissipation. The dissipative term is responsible to the irreversible work as discussed in the "Work" section. The rate of dissipation is $\dot{\mathcal{W}} = \eta \dot{X}^2$.

The above considerations regarding dissipation can be generalized to a source that has an arbitrary power spectrum ("AC driving"). The irreversible work equals the integral over $\eta(\omega)\dot{X}_\omega^2$. For a stationary driving source \dot{X}_ω^2 is proportional to the measurement time. So we can write

$$\dot{\mathcal{W}} = \int_{-\infty}^{\infty} \eta(\omega) \tilde{S}_{\text{source}}(\omega) \frac{d\omega}{2\pi} \equiv \bar{\eta}_{AC} \times \text{RMS}[\dot{X}]^2 \quad (549)$$

Possibly it is more transparent to consider a pure AC source that has a definite frequency Ω . In such a case we write

$$X(t) = \text{Re}[Ae^{-i\Omega t}] \quad (550)$$

$$\langle \mathcal{F} \rangle_t = \text{Re}[\chi(\Omega) Ae^{-i\Omega t}] = \chi_0(\Omega)X - \eta(\Omega)\dot{X} \quad (551)$$

$$\dot{\mathcal{W}} = \langle -\dot{X}\mathcal{F} \rangle_t = \eta(\Omega) \times (1/2)[A\Omega]^2, \quad [\text{averaged over cycle}] \quad (552)$$

Note again that only the out-of-phase response gives dissipation, and that $A\Omega/\sqrt{2}$ is the RMS value of sinusoidal driving.

===== [12.3] LRT with several variables

Commonly the Hamiltonian $\mathcal{H}(\mathbf{r}, \mathbf{p}; X_1, X_2, X_3)$ depends on several control parameters. Then we can define generalized forces in the usual way:

$$\mathcal{F}^k = -\frac{\partial \mathcal{H}}{\partial X_k} \quad (553)$$

It is implicit above that the X_j represent some small deviation from some initial value $X(0) = X_0 = 0$. Consequently the postulated linear response relation is written as

$$\langle \mathcal{F}^k \rangle_t = \sum_j \int_{-\infty}^{\infty} \alpha^{kj}(t-t') X_j(t') dt' \quad (554)$$

The low frequency limit of the linear relation between the generalized forces and the *rate* of the driving can be regarded as a generalized Ohm law that includes an additional "geometric" term. Disregarding the conservative contribution and changing notation for the dissipation coefficient the one parameter version $\langle \mathcal{F} \rangle = -G\dot{X}$ is generalized as follows:

$$\langle \mathcal{F}^k \rangle = -\sum_j \mathbf{G}^{kj} \dot{X}_j = -\boldsymbol{\eta} \dot{\mathbf{X}} - \mathbf{B} \wedge \dot{\mathbf{X}} \quad (555)$$

where $\boldsymbol{\eta}^{kj}$ and \mathbf{B}^{kj} are the symmetric and anti-symmetric parts of \mathbf{G}^{kj} . The rate of dissipation is given by

$$\dot{\mathcal{W}} = -\sum_k \langle \mathcal{F}^k \rangle \dot{X}_k = \sum_{k,j} \boldsymbol{\eta}_{kj} \dot{X}_k \dot{X}_j \quad (556)$$

Note that only $\boldsymbol{\eta}^{kj}$ contributes to the dissipation.

===== [12.4] The Kubo formula

The Kubo formula is an expression for the response kernel that relates the expectation value $\langle A \rangle_t$ of some observable A to driving field $f(t)$, where the driving term in the Hamiltonian $-f(t)B$ involves the operator B .

$$\alpha^{AB}(t) = \Theta(t) \left\langle \frac{i}{\hbar} [A(t), B] \right\rangle \equiv \Theta(t) \tilde{K}^{AB}(t) \quad [\text{Kubo formula}] \quad (557)$$

The formula has a good classical limit, and has various derivations. See "Lecture notes in quantum mechanics". The DC value of the dissipation coefficient is obtained by integration:

$$\eta^{AB} \text{ [DC limit]} = \int_0^\infty K^{AB}(\tau) \tau d\tau \quad (558)$$

More generally, an expression for the generalized susceptibility follows from the convolution theorem:

$$\chi^{AB}(\omega) \equiv \text{FT}[\alpha^{AB}(\tau)] = \int_{-\infty}^\infty \frac{i\tilde{K}^{AB}(\omega')}{\omega - \omega' + i0} \frac{d\omega'}{2\pi} \quad (559)$$

Of particular interest is the case where $A = B = \mathcal{F}$ is a generalized force that is conjugate to the variation of some parameter X such that $f(t) = (X(t) - X_0)$. This is the case of interest in the study of friction (where \dot{f} is the displacement velocity) and in the study of electrical conductance (where \dot{f} is the electromotive field). From the definition it follows that $K(-\tau) = -K(\tau)$, hence $K(\omega)$ is pure imaginary, and consequently the friction coefficient is

$$\eta(\omega) \equiv \frac{\text{Im}[\chi(\omega)]}{\omega} = \frac{1}{i2\omega} \tilde{K}(\omega) \quad [\text{Kubo formula for the dissipation coefficient}] \quad (560)$$

So far we have used versions of the Kubo formula that are "good" both classically and quantum mechanically. In the quantum case one can write a version of this formula that involves the non-symmetrized correlation function:

$$\eta(\omega) = \frac{1}{2\hbar\omega} [S(\omega) - S(-\omega)] \quad [\text{Quantum FGR version of the Kubo formula}] \quad (561)$$

This expression can be deduced directly from the FGR picture as follows. Assume that $\mathcal{H}_{\text{driving}} = -f(t)V$ with $f(t) = A \sin(\Omega t)$. From the FGR it follows that the rate of energy absorption due to upward transitions is $(A/2)^2 \tilde{S}(\Omega)\Omega$. Similarly the rate of energy emission is $(A/2)^2 \tilde{S}(-\Omega)\Omega$. The net rate of heating is the difference. By definition it is written as $\dot{\mathcal{W}} = \eta(\Omega) \overline{[\dot{f}^2]}$, where $\overline{[\dot{f}^2]} = (1/2)[A\Omega]^2$. Hence one deduce the above expression for η .

Below we discuss the non-trivial generalization of the Kubo linear response formalism for the case of Hamiltonian that depends on several parameters. We start with the dissipation-less quantum adiabatic limit, and continue with the full linear response analysis.

===== [12.5] Adiabatic response

For an extended presentation see "Lecture notes in quantum mechanics". Given an Hamiltonian $\mathcal{H}(\mathbf{r}, \mathbf{p}; X_1, X_2, X_3)$ that depends on several control parameters, we find the adiabatic basis $|n(X)\rangle$ with eigenenergies $E_n(X)$. Then, for a given level, we define in parameter space the "Christoffel symbols" and the associated "curvature field" as follows:

$$\mathbf{A}_{nm}^j = i\hbar \left\langle n(X) \left| \frac{\partial}{\partial X_j} m(X) \right. \right\rangle \quad (562)$$

$$\mathbf{B}_n^{ij} = \partial_i \mathbf{A}_n^j - \partial_j \mathbf{A}_n^i \quad (563)$$

We use the notation $\mathbf{A}_n^j = \mathbf{A}_{nn}^j$, and note the following identities:

$$\mathbf{A}_{nm}^j = \frac{-i\hbar \mathcal{F}_{mn}^j}{E_m - E_n} \quad [n \neq m] \quad (564)$$

$$\mathbf{B}_n^{ij} = \sum_{m(\neq n)} \frac{2\hbar \text{Im} [\mathcal{F}_{nm}^i \mathcal{F}_{mn}^j]}{(E_m - E_n)^2} \quad (565)$$

If we have 3 control variables it is convenient to use notations suggesting that we can formally regard \mathbf{A}_n as a vector potential whose rotor \mathbf{B}_n is formally like a magnetic field:

$$\mathbf{X} \mapsto (X_1, X_2, X_3) \quad (566)$$

$$\mathbf{A} \mapsto (A_{nn}^1, A_{nn}^2, A_{nn}^3) \quad (567)$$

$$\mathbf{B} \mapsto (B^{23}, B^{31}, B^{12}) \quad (568)$$

With the above definitions we can cast the Schrodinger equation into a very convenient form. This is done as follows. We write

$$\frac{d}{dt}|\psi\rangle = -\frac{i}{\hbar}\mathcal{H}(X(t))|\psi\rangle \quad (569)$$

We expand the state in the adiabatic basis as

$$|\psi\rangle = \sum_n a_n(t) |n(X(t))\rangle \quad (570)$$

and get the equation

$$\frac{da_n}{dt} = -\frac{i}{\hbar}(E_n - \dot{\mathbf{X}} \cdot \mathbf{A}_n)a_n - \frac{i}{\hbar} \sum_m \mathbf{W}_{nm} a_m \quad (571)$$

where

$$\mathbf{W}_{nm} \equiv - \sum_j \dot{\mathbf{X}}_j \mathbf{A}_{nm}^j \quad \text{for } n \neq m, \text{ else zero} \quad (572)$$

In the adiabatic limit the first order response of a system that has been prepared in the n th adiabatic state is

$$\langle \mathcal{F}^k \rangle = - \sum_j \mathbf{B}_n^{kj} \dot{\mathbf{X}}_j = -\mathbf{B} \wedge \dot{\mathbf{X}} \quad (573)$$

We shall explain in the next section that this corresponds to the geometric part of the response in the Kubo formula. The Kubo formula contains an additional non-adiabatic (dissipative) term that reflects FGR transitions between levels.

===== [12.6] Low frequency response

Here we go beyond adiabatic response and discuss both the adiabatic and dissipative terms that are implied by the Kubo formula. Recall that the Kubo expression for the response kernel is $\alpha^{kj}(\tau) = \Theta(\tau) K^{kj}(\tau)$, whose Fourier transform is the generalized susceptibility:

$$\chi^{kj}(\omega) = \int_{-\infty}^{\infty} \frac{i\tilde{K}^{kj}(\omega')}{\omega - \omega' + i0} \frac{d\omega'}{2\pi} \quad (574)$$

Taking into account that $\text{Re}[\chi^{kj}(\omega)]$ is symmetric with respect to ω we have

$$\mathbf{G}^{kj} = \lim_{\omega \rightarrow 0} \frac{\text{Im}[\chi^{kj}(\omega)]}{\omega} = \lim_{\omega \rightarrow 0} \frac{d}{d\omega} \chi^{kj}(\omega) = \int_0^{\infty} K^{kj}(\tau) \tau d\tau \quad (575)$$

The last expression (in time domain) is mentioned for completeness. In practice it is more convenient to proceed in frequency domain. After some straightforward algebra we get

$$\mathbf{G}^{kj} = \frac{1}{2} \lim_{\omega \rightarrow 0} \frac{\text{Im}[\tilde{K}^{kj}(\omega)]}{\omega} - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{\text{Re}[\tilde{K}^{kj}(\omega)]}{\omega^2} \equiv \boldsymbol{\eta}^{kj} + \mathbf{B}^{kj} \quad (576)$$

We notice that $\boldsymbol{\eta}^{kj}$ is a symmetric matrix while \mathbf{B}^{kj} is anti-symmetric. Hence in abstract notation the linear-response relation can be written as a generalized Ohm law:

$$\langle \mathcal{F}^k \rangle = - \sum_j \mathbf{G}^{kj} \dot{X}_j = -\boldsymbol{\eta} \dot{\mathbf{X}} - \mathbf{B} \wedge \dot{\mathbf{X}} \quad (577)$$

This is a generalization of the adiabatic response formula. The additional term takes into account the FGR non-adiabatic transitions between levels. To see clearly the connection we substitute the spectral decomposition of $\tilde{K}^{kj}(\omega)$ and get the following expressions:

$$\chi^{kj}(\omega) = \int_{-\infty}^{\infty} \frac{i\tilde{K}^{kj}(\omega')}{\omega - \omega' + i0} \frac{d\omega'}{2\pi} = \sum_n p_n \sum_m \left(\frac{-\mathcal{F}_{nm}^k \mathcal{F}_{mn}^j}{\hbar\omega - (E_m - E_n) + i0} + \frac{\mathcal{F}_{nm}^j \mathcal{F}_{mn}^k}{\hbar\omega + (E_m - E_n) + i0} \right) \quad (578)$$

and

$$\boldsymbol{\eta}^{kj} = \frac{1}{2} \lim_{\omega \rightarrow 0} \frac{\text{Im}[\tilde{K}^{kj}(\omega)]}{\omega} = -\pi\hbar \sum_{n,m} \frac{f(E_n) - f(E_m)}{E_n - E_m} \mathcal{F}_{nm}^k \mathcal{F}_{mn}^j \delta(E_m - E_n) \quad (579)$$

$$\mathbf{B}^{kj} = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{\text{Re}[\tilde{K}^{kj}(\omega)]}{\omega^2} = \sum_{n,m} (f(E_n) - f(E_m)) \frac{-i\hbar \mathcal{F}_{nm}^k \mathcal{F}_{mn}^j}{(E_m - E_n)^2} \quad (580)$$

The $\text{Re}[\]$ and $\text{Im}[\]$ are not required because the doubles summation cares for that. To expression for \mathbf{B}^{kj} can be written in a way that better emphasize the relation to the analysis of the adiabatic response:

$$\mathbf{B}^{kj} = \sum_n f(E_n) \sum_{m(\neq n)} \frac{2\hbar \text{Im}[\mathcal{F}_{nm}^k \mathcal{F}_{mn}^j]}{(E_m - E_n)^2} = \sum_n f(E_n) \mathbf{B}_n^{kj} \quad (581)$$

[13] The fluctuation dissipation relation

===== [13.1] General formulation

The essence of the fluctuation dissipation (FD) relation is to relate the response of a system to its fluctuations in equilibrium. In order to derive this relation we have to supply information on the preparation of the system, which is typically assumed to be canonical. In the classical context there is a useful microcanonical version from which the canonical version can be derived. The standard formal derivation of the FD relation is based on the generalized detailed balance relation that allows to express $\tilde{K}^{kj}(\omega)$ using $\tilde{C}^{kj}(\omega)$. There are two useful cases: DC version for any number of variables, and AC version for one parameter driving. In the DC case we know from Kubo that G is an integral over $\tau K(\tau)$, and from the detailed balance relation that $K(\tau)$ can be obtained from the derivative of $C(\tau)$. After integration by parts we get

$$G^{AB} = \frac{1}{T} \int_0^\infty C^{AB}(\tau) d\tau \quad (582)$$

We turn now to the one-parameter driving AC version. Here we realize that the imaginary part of the susceptibility is determined by $\tilde{K}(\omega)$, and hence from the detailed balance relation it follows that

$$\frac{\text{Im}[\chi(\omega)]}{\omega} = \frac{1}{\hbar\omega} \tanh\left(\frac{\hbar\omega}{2T}\right) \tilde{C}(\omega) \quad (583)$$

Both versions, the DC and the AC are consistent and imply that the low frequency dissipation coefficient is related to the equilibrium intensity of the fluctuations:

$$\eta = \frac{\nu_T}{2T}, \quad \nu_T \equiv \int_{-\infty}^\infty \langle \mathcal{F}(\tau) \mathcal{F}(0) \rangle_T d\tau \quad (584)$$

Note that in the above writing we assume that the equilibrium value of the fluctuating force is $\langle \mathcal{F} \rangle = 0$, else \mathcal{F} should be re-defined so as to have a zero average.

===== [13.2] The diffusion-dissipation picture

We can illuminate the physics of FD for DC driving using a simple diffusion-dissipation picture. We show below that the DC energy absorption rate is related to the induced diffusion in energy space. To simplify the presentation we use a classical language. We can deduce that the driving induces diffusion in energy space from the relation

$$E(t) - E(0) = -\dot{X} \int_0^t \mathcal{F}(t') dt' \quad (585)$$

leading to

$$\langle (E(t) - E(0))^2 \rangle = \dot{X}^2 \int_0^t \int_0^t \langle \mathcal{F}(t') \mathcal{F}(t'') \rangle dt' dt'' \quad (586)$$

where the averaging assumes a microcanonical preparation. Thus we get

$$\delta E^2(t) = 2D_E t \quad (587)$$

where the leading order estimate for the diffusion is

$$D_E = \frac{1}{2} \dot{X}^2 \int_{-\infty}^\infty \langle \mathcal{F}(\tau) \mathcal{F}(0) \rangle_E d\tau = \frac{1}{2} \nu_E \dot{X}^2 \quad (588)$$

On long times we assume that the probability distribution $\rho(E) = g(E)f(E)$ of the energy satisfies the following diffusion equation:

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial E} \left(g(E) D_E \frac{\partial}{\partial E} \left(\frac{1}{g(E)} \rho \right) \right) \quad (589)$$

The energy of the system is $\langle \mathcal{H} \rangle = \int E \rho(E) dE$. Taking the time derivative and integrating by parts, it follows that the rate of energy absorption is

$$\dot{\mathcal{W}} = \frac{d}{dt} \langle \mathcal{H} \rangle = - \int_0^\infty dE g(E) D_E \frac{\partial}{\partial E} \left(\frac{\rho(E)}{g(E)} \right) \quad (590)$$

For a microcanonical preparation $\rho(E) = \delta(E - \mathcal{E})$. Substitution and integration by parts leads to

$$\dot{\mathcal{W}} = \frac{d}{dt} \langle \mathcal{H} \rangle = \frac{1}{g(E)} \frac{d}{dE} [g(E) D_E] \Big|_{E=\mathcal{E}} \quad (591)$$

By definition $\dot{\mathcal{W}} = \eta \dot{X}^2$ and $D_E = (1/2)\nu \dot{X}^2$. Consequently the diffusion-dissipation relation reduces immediately to the microcanonical version of the fluctuation-dissipation relation:

$$\eta = \frac{1}{2} \frac{1}{g(E)} \frac{d}{dE} [g(E) \nu_E] \quad (592)$$

The canonical version $\eta = \nu_T/(2T)$ can be derived from the integral expression for $\dot{\mathcal{W}}$, upon the substitution $\rho(E) = (1/Z)g(E)e^{-\beta E}$. Optionally it can be obtained from the microcanonical version by canonically averaging over E and performing integration by parts.

===== [13.3] The wall formula

The first prototype application of the FD relation is to the calculation of the friction in the Brownian motion problem. Consider a gas of particles in a box. The system is driven by moving in it a "spoon", or a "piston" or a "Brownian body".

- The parameter in $\mathcal{H}(X)$ represents the position of the spoon.
- The generalized force is the Newtonian force $\langle \mathcal{F} \rangle$ on the spoon.
- The DC linear response relation $\langle \mathcal{F} \rangle = -\eta \dot{X}$ describes friction.
- The dissipation rate is $\dot{\mathcal{W}} = \eta \dot{X}^2$.

Our purpose below is to find an expression for the friction coefficient η using the FD relation. For this purpose we have to calculate the intensity ν_T of the fluctuations of \mathcal{F} at equilibrium, and to use the relation $\eta = \nu_T/(2T)$.

Due to random collisions of the gas particles, the Brownian body experiences a "random force" that can be written as the sum of short impulses:

$$F(t) = \sum_j 2m v_j \delta(t - t_j) \quad (593)$$

Here t_j is the time of the j th collision with velocity v_j at the x direction. Note that $|v_j| \sim v_T$, where $v_T = (2T/m)^{1/2}$ is the thermal velocity. The rate of collision for N particles is

$$\frac{1}{\tau_0} = N \times \left(\frac{A}{L^2} \right) \times \frac{v_T}{L} \quad (594)$$

where L^3 is the volume of the box that holds the gas particles, and A is the effective area of the moving wall. Accordingly the intensity of fluctuations is

$$\nu_T = \tilde{C}(\omega=0) = \frac{1}{\tau_0}(\mathbf{m}v_T)^2 = \mathbf{m}^2 v_T^3 \frac{N}{L^3} A \quad (595)$$

and for the friction we get

$$\eta = \frac{1}{2T} \tilde{C}(\omega=0) = \rho v_T \times A \quad (596)$$

where $\rho = (N/L^3)\mathbf{m}$ is the mass density of the gas particles.

We note that if the dynamics of the Brownian body is described by a Langevin equation, then $\nu/\eta = 2T$ implies that a canonical equilibrium is reached. For more details see the Langevin section. This was in fact the historical deduction of the FD relation by Einstein in the context of Brownian motion study. If the Brownian particle is moving in an incompressible fluid the above result does not apply. Instead the friction is given by Stokes Law, and we can use the FD relation "in reverse" in order to deduce the intensity of fluctuations.

===== [13.4] The Drude formula

The second prototype application of the FD relation is to the calculation of electrical conductance. Here we show how to derive the Drude formula for a gas of classical particles in an EMF driven ring. For an extended discussion of electrical conductance see the "additional topics" section of the lecture notes.

We consider a ring driven by an electro-motive force (EMF). The interaction term originates from the kinetic term $[p - (e/L)\Phi(t)]^2/(2\mathbf{m})$, where Φ is the flux and $I = (e/L)v$ is the conjugate current. Optionally we can say the the interaction is $-A(t)v$, where $A(t)$ is the vector potential and the velocity v is the conjugate variable. Summarizing:

- The parameter in $\mathcal{H}(\Phi)$ represents the magnetic flux.
- The generalized force is the current $\langle \mathcal{I} \rangle$ in the ring.
- The rate in which the flux is varied determines the EMF $= -\dot{\Phi}$ by Faraday law.
- The DC linear response relation $\langle \mathcal{I} \rangle = G \times \text{EMF}$ is Ohm law.
- The dissipation rate $\dot{\mathcal{W}} = G\dot{\Phi}^2$ describes Joule heating.

Our purpose below is to find an expression for the conductance G using the FD relation. For this purpose, following Drude, we postulate what is the velocity-velocity correlation function; calculate the intensity ν_T of the fluctuations of \mathcal{I} at equilibrium, and use the relation $G = \nu_T/(2T)$.

Following Drude we assume an exponential velocity-velocity correlation function with a time constant τ_0 , such that the mean free path is $\ell = v_T \tau_0$. Hence we deduce that $\tilde{C}_{vv}(\omega)$ is a Lorentzian, and in particular

$$D = \frac{1}{2} \tilde{C}_{vv}(0) = v_T^2 \tau_0 \quad (597)$$

where $v_T = (2T/\mathbf{m})$ is the thermal velocity. From here we get an expression for the intensity of the current fluctuations

$$\nu_T = \tilde{C}(\omega=0) = \left(\frac{e}{L}\right)^2 \tilde{C}_{vv}(0) \quad (598)$$

and for the conductance of N particles we get

$$G^{[N]} = \frac{N}{2T} \tilde{C}(\omega=0) = \frac{N}{L^2} \frac{e^2}{\mathbf{m}} \tau_0 \equiv \frac{A}{L} \sigma \quad (599)$$

where A is the cross section of the ring. Optionally the Drude expression can be written as

$$G^{[N]} = e^2 \left(\frac{N}{mvL} \right) \frac{\ell}{L} \equiv \frac{e^2}{2\pi} \mathcal{M} \frac{\ell}{L} \quad (600)$$

where \mathcal{M} corresponds to the effective number of open modes. There is a very simple toy model for which the "exponential" velocity-velocity correlation can be deduced, and hence ℓ/L can be evaluated analytically. Consider a ring with a single stochastic scatterer that has a transmission g . The current-current correlation function at given energy is

$$C(t) = e^2 \frac{v_E}{L} \sum_{n=-\infty}^{\infty} (2g-1)^n \delta \left(t - \left(\frac{L}{v_E} n \right) \right) \quad [\text{exponential decay of correlations}] \quad (601)$$

From the integral it follows that

$$\frac{\ell}{L} = \frac{g}{1-g} \quad (602)$$

Assuming that g is independent of energy the result applies to any occupation.

Conductor in electric field.— A straightforward generalization of the above applies for an extended piece of metal that is placed in a time dependent electric field. The electric field is described by a vector potential such that $\mathcal{E} = -\dot{A}$. The interaction term in the Hamiltonian is an extended version of the simplified $-A(t)v$ that we have assumed in previous discussion:

$$\mathcal{H}_{\text{int}} = - \int J(x) \cdot A(x) d^3x \quad (603)$$

In linear response theory the current is proportional to the rate in which the parameters are being changed in time. Regarding the values of A at different points in space as independent parameters the postulated linear response relation takes the form

$$\langle J(x) \rangle = \int \sigma(x, x') \mathcal{E}(x') d^3x \quad (604)$$

where $\sigma_{ij}(x, x')$ is called the conductivity matrix. The FD relation states that the conductivity is proportional to the temporal FT of $\langle J_i(x, t) J_j(x', t') \rangle$ with respect to the time difference $\tau = t - t'$. The proportionality constant is $1/(2T)$ in the DC limit.

Nyquist Noise.— The FD relation in the electrical context is known as Nyquist theorem. It can be used "in reverse" in order to deduce the Nyquist noise $\nu = 2GT$, provided G is known from experiment. It should be clear that in non-equilibrium conditions we might have extra fluctuations, which in this example are known as *shot noise*.

===== [13.5] Forced oscillator and forced particle

Consider a particle that is (say) bounded to a spring. This means harmonic oscillator that is characterized by frequency Ω . The interaction term is $-\mathcal{E}(t)x$. Accordingly,

- The parameter in $\mathcal{H}(\mathcal{E})$ represents an electric field.
- The generalized force is the polarization $\langle x \rangle$ of the particle.
- The AC linear response relation is $\langle x \rangle = \chi(\omega) \mathcal{E}$.

The FD relation implies that x has fluctuations at equilibrium, that are related to the imaginary part of the susceptibility:

$$\tilde{C}_{xx}(\omega) = \hbar \coth \left(\frac{\hbar\omega}{2T} \right) \text{Im} [\chi(\omega)], \quad \chi(\omega) = \frac{1}{-m\omega^2 - i\eta\omega + m\Omega^2} \quad (605)$$

Note that the fluctuations of the velocity are $\tilde{C}_{vv}(\omega) = \omega^2 \tilde{C}_{xx}(\omega)$. From $\tilde{C}_{xx}(0)$ and $\tilde{C}_{vv}(0)$ one can deduce the average energy of the oscillator and verify that it is in agreement with the canonical ensemble.

Forced particle.— The limit $\Omega \rightarrow 0$ of harmonic oscillator corresponds formally to a Brownian particle. Accordingly in the classical limit we get a Lorentzian

$$\tilde{C}_{vv}(\omega) = (2T/m) \times \frac{(\eta/m)}{\omega^2 + (\eta/m)^2} \quad (606)$$

indicating a Drude type (exponential) velocity-velocity correlation function. The integral over the velocity-velocity correlation function determined the diffusion coefficient, namely

$$D = \frac{1}{2} \tilde{C}_{vv}(0) = \frac{T}{\eta} \quad (607)$$

There is an optional shortcut in the application of the FD relation in the context of forced particle. Let us write the electric field as $\mathcal{E} = -\dot{A}$. The interaction term is $-A(t)v$. Accordingly,

- The parameter in $\mathcal{H}(A)$ represents the vector potential.
- The generalized force is the velocity $\langle v \rangle$ of the particle.
- The DC linear response relation $\langle v \rangle = \mu \mathcal{E}$ describes drift motion.
- The dissipation rate $\dot{\mathcal{W}} = \mu \dot{\mathcal{E}}^2$ describes Joule heating.

The FD relation in this notations implies that v has fluctuations at equilibrium, that are related to the mobility $\mu = 1/\eta$. The "intensity" of the velocity fluctuations is $2D$. Hence the classical FD relation implies that the ratio of the diffusion (D) to the mobility (μ) equals the temperature (T). This is known as Einstein relation. For more details see the Langevin section.

===== [13.6] The fluctuations of an Ohmic system

Sometimes it is convenient to characterize the system by its response, and from this to deduce the power spectrum of the fluctuations. So we regard $\tilde{K}(\omega)$ as the input and write

$$\tilde{C}(\omega) = \frac{\hbar}{2} \coth\left(\frac{\hbar\omega}{2T}\right) \text{Im} [\tilde{K}(\omega)] \quad (608)$$

$$\tilde{S}(\omega) = \frac{\tilde{C}(\omega)}{\cosh(\hbar\omega/2T)} \exp\left(\frac{\hbar\omega}{2T}\right) \quad (609)$$

The so called Ohmic power spectrum is

$$\tilde{K}_{\text{ohmic}}(\omega) = i2\eta\omega \quad (610)$$

$$\tilde{C}_{\text{ohmic}}(\omega) = \eta\hbar\omega \coth\left(\frac{\hbar\omega}{2T}\right) \quad (611)$$

$$\tilde{S}_{\text{ohmic}}(\omega) = \eta\hbar\omega \frac{2}{1 - e^{-\hbar\omega/T}} \quad (612)$$

for which the friction coefficient is $\eta = \text{const}$, up to some implicit high frequency cutoff ω_c , and the intensity of fluctuations is $\nu = 2\eta T$.

===== [13.7] Many body fluctuations of Fermions

It is interesting to see how an Ohmic behavior is deduced for a low temperature system of Fermions. We consider the fluctuations of a general observable A . If we treat the many body system as a whole then we have to employ second

quantization to write $\hat{\mathbf{A}} = \sum_{mn} A_{mn} a_m^\dagger a_n$. Excluding the irrelevant diagonal $n=m$ terms we get for a non-interacting system in a thermal state

$$\begin{aligned}
\tilde{S}^{[N]}(\omega) &= \text{FT} \left\langle \hat{\mathbf{A}}(t) \hat{\mathbf{A}}(0) \right\rangle \\
&= \sum_{nm} |A_{mn}|^2 \left\langle a_n^\dagger a_m a_m^\dagger a_n \right\rangle 2\pi \delta(\omega - (E_m - E_n)) \\
&= \sum_{nm} (1 - f(E_m)) f(E_n) |A_{mn}|^2 2\pi \delta(\omega - (E_m - E_n)) \\
&= \int \frac{dE}{\Delta} (1 - f(E + \omega)) f(E) \tilde{C}_E(\omega) \\
&= \frac{\omega/\Delta}{1 - e^{-\omega/T}} \tilde{C}_{E_F}(\omega)
\end{aligned} \tag{613}$$

where the last expression is obtained if the single particle power spectrum is energy independent in the range of interest around the Fermi energy. Note that, at zero temperature, the first factor becomes $(\omega/\Delta)\Theta(\omega)$, cutting off all contributions at negative frequencies. Physically, this represents the fact that a zero-temperature fermion system can only absorb energy. If it couples to a zero-temperature environment, there will not be any transitions at all, in contrast to what would be deduced from the single-particle spectrum alone.

===== [13.8] The FD relation for a system of Fermions

For one particle we can define the single particle microcanonical fluctuation spectrum $C_E(\omega)$, and the canonical fluctuation spectrum $C_T(\omega)$. If we have many body occupation by N Fermions, we can express the additive $K(\omega)$ using the one-particle correlation functions (The commutator is additive and does not care about the Pauli exclusion principle):

$$\tilde{K}^{[N]}(\omega) = i\omega \times \begin{cases} g(E_F) \tilde{C}_{E_F}(\omega) & \text{degenerated Fermi occupation} \\ (N/T) \tilde{C}_T(\omega) & \text{dilute Boltzman occupation} \end{cases} \tag{614}$$

Once we know $\tilde{K}^{[N]}(\omega)$ we can calculate the dissipation coefficient using the Kubo formula:

$$\eta^{[N]}(\omega) = \frac{1}{i2\omega} \tilde{K}^{[N]}(\omega) \tag{615}$$

The fluctuations of the many body current are deduced from the canonical FD relation:

$$\tilde{C}^{[N]}(\omega) = \frac{\hbar}{2} \coth\left(\frac{\hbar\omega}{2T}\right) \text{Im} \left[\tilde{K}^{[N]}(\omega) \right] = \frac{\hbar\omega}{2T} \coth\left(\frac{\hbar\omega}{2T}\right) \begin{cases} (T/\Delta) \tilde{C}_{E_F}(\omega) \\ N \tilde{C}_T(\omega) \end{cases} \tag{616}$$

Note that for the non-symmetrized power spectrum $\tilde{S}^{[N]}(\omega)$ we have the same expression with

$$\coth\left(\frac{\hbar\omega}{2T}\right) \mapsto \frac{2}{1 - e^{-\hbar\omega/T}} \tag{617}$$

It is important to observe that the intensity ν of the current fluctuations is not simply the one-particle ν times the number of particles. Rather, for low temperature Fermi occupation, the effective number of particles that contribute to the noise is T/Δ where Δ is the mean level spacing. Needless to say that the result for $\tilde{S}^{[N]}(\omega)$ that has been deduced here from the FD relation is consistent with the direct calculation utilizing Fock space formalism of the previous section.

===== [13.9] The fluctuations of the potential in metals

The dielectric constant of a metal is defined via the linear relation between the total electrostatic potential U_{total} and an external test charge density ρ_{ext}

$$U_{\text{total}} = \frac{1}{\varepsilon(q, \omega)} \left(\frac{4\pi e^2}{q^2} \right) \rho_{\text{ext}} \quad (618)$$

For simplicity we relate here and below to one component q of the fields. The total electrostatic potential is the sum of the external potential $U_{\text{ext}} = (4\pi e^2/q^2)\rho_{\text{ext}}$, and the induced potential $U_{\text{elct}} = (4\pi e^2/q^2)\rho_{\text{elct}}$, where ρ_{elct} is the total density of the electrons. The dielectric constant can be deduced from the equations of motion $\partial\rho_{\text{elct}}/\partial t = -\nabla J$ with $J = -(\sigma/e^2)\nabla U_{\text{total}} - D\nabla\rho_{\text{elct}}$ that leads to the relation

$$\rho_{\text{elct}} = \frac{(\sigma/e^2)q^2}{i\omega - Dq^2} U_{\text{total}} \quad (619)$$

and hence to $U_{\text{total}} = (1/\varepsilon)U_{\text{ext}}$, where

$$\varepsilon(q, \omega) = 1 - \frac{4\pi\sigma}{i\omega - Dq^2}. \quad (620)$$

Note that

$$\text{Im} \left[\frac{-1}{\varepsilon(q, \omega)} \right] = \frac{4\pi\sigma\omega}{(Dq^2 + 4\pi\sigma)^2 + \omega^2} \approx \frac{\omega}{4\pi\sigma} \quad (621)$$

The interaction between the electrons and an external electrostatic field is described by $\mathcal{H}_{\text{ext}} = U_{\text{ext}}\rho_{\text{elct}}$ which can be also written as $\mathcal{H}_{\text{ext}} = \rho_{\text{ext}}U_{\text{elct}}$. The fluctuation dissipation relation expresses $\tilde{S}^{[N]}(q, \omega)$ using the response function $\alpha(\mathbf{q}, \omega)$ that relates U_{elct} to $-\rho_{\text{ext}}$ which is

$$\alpha(\mathbf{q}, \omega) = \frac{4\pi e^2}{q^2} \left[1 - \frac{1}{\varepsilon(\mathbf{q}, \omega)} \right] \quad (622)$$

Namely,

$$\tilde{S}^{[N]}(\mathbf{q}, \omega) = \text{Im} \left[\alpha(\mathbf{q}, \omega) \right] \left(\frac{2}{1 - e^{-\omega/T}} \right) \quad (623)$$

leading to

$$\tilde{S}^{[N]}(\mathbf{q}, \omega) \approx \frac{e^2}{\sigma} \frac{1}{q^2} \left(\frac{2\omega}{1 - e^{-\omega/T}} \right) \quad (624)$$

The Ohmic behavior is cut-off by $|\omega| \lesssim 1/\tau_c$ and $|\mathbf{q}| \lesssim 1/\ell$ where $\ell = v_F\tau_c$ is the elastic mean free path, and v_F is the Fermi velocity. Recalling the Einstein relation $\sigma = e^2\nu D$, where $\nu = \Delta^{-1}/L^d$ is the density of states per unit volume, we can write this result more conveniently as follows:

$$\tilde{S}^{[N]}(\mathbf{q}, \omega) \approx \frac{1}{\nu D q^2} \left(\frac{2\omega}{1 - e^{-\omega/T}} \right) \quad (625)$$

Note that the electron charge e cancels out from this final result for the Nyquist noise spectrum. This well-known fact is due to the effects of screening: A larger value of the charge would be canceled by a correspondingly stronger suppression of density fluctuations.

System interacting with a bath

[14] The modeling Hamiltonian

===== [14.1] The Born-Oppenheimer Hamiltonian

We first discuss system that is coupled to some other degrees of freedom that can be eliminated using an adiabatic scheme. This leads to the Born-Oppenheimer picture. It is strongly related to Linear response theory, and the presentation below is arranged accordingly.

Linear response theory is the leading formalism to deal with driven systems. Such systems are described by a Hamiltonian

$$\mathcal{H} = \mathcal{H}(\mathbf{Q}, \mathbf{P}; X(t)) \quad (626)$$

where (\mathbf{Q}, \mathbf{P}) is a set of canonical coordinates (in case that the Hamiltonian is the outcome of "quantization"), and $X(t)$ is a set of time dependent classical parameters ("fields"). For example, X can be the position of a piston. In such case \dot{X} is its velocity. More interesting is the case where X is the magnetic flux through a ring. In such a case \dot{X} is the electro motive force. The Kubo formula allows the calculation of the response coefficients. In the mentioned examples these are the "friction coefficient" and the "conductance of the ring" respectively.

In the limit of a very slow time variation (small \dot{X}), linear response theory coincides with the "adiabatic picture". In this limit the response of the system can be described as a non-dissipative "geometric magnetism" effect (this term was coined by Berry and Robbins). If we increase \dot{X} beyond a certain threshold, then we get Fermi-golden-rule transitions between levels, leading to absorption of energy ("dissipation"). Then linear response theory can be regarded as a generalization of "Ohm law".

The Born-Oppenheimer picture allows to deal with Hamiltonians of the type

$$\mathcal{H}_{\text{total}} = \mathcal{H}_0(x, p) + \mathcal{H}(\mathbf{Q}, \mathbf{P}; x) \quad (627)$$

Here we replaced the parameter $X(t)$ by a dynamical variable x . The standard textbook example is the study of diatomic molecules. In such case x is the distance between the nuclei. It is evident that the theory of driven systems is a special limit of this problem, which is obtained if we treat x as a classical variable. For presentation purpose let us consider the Hamiltonian

$$\mathcal{H}_{\text{total}} = \frac{1}{2M} \sum_j p_j^2 + \mathcal{H}(\mathbf{Q}, \mathbf{P}; x) \quad (628)$$

We define the basis $|x, n(x)\rangle = |x\rangle \otimes |n(x)\rangle$, and expand the state as

$$|\Psi\rangle = \sum_{n,x} \Psi_n(x) |x, n(x)\rangle \quad (629)$$

Using

$$\langle x, n(x) | \mathcal{H} | x_0, m(x_0) \rangle = \delta(x-x_0) \times \delta_{nm} E_n(x) \quad (630)$$

$$\langle x, n(x) | p_j | x_0, m(x_0) \rangle = (-i\partial_j \delta(x-x_0)) \times \langle n(x) | m(x_0) \rangle = -i\partial_j \delta(x-x_0) \delta_{nm} - \delta(x-x_0) \mathbf{A}_{nm}^j(x) \quad (631)$$

we deduce that $p_j \mapsto -i\partial_j - \mathbf{A}_{nm}^j(x)$, and the Hamiltonian can be written as

$$\mathcal{H}_{\text{total}} = \frac{1}{2M} \sum_j (p_j - \mathbf{A}^j(x))^2 + \mathbf{E}(x) \quad (632)$$

The adiabatic approximation is obtained if one neglects the $n \neq m$ terms that couple the motion on different energy surfaces. These couplings are responsible to the dissipation effect.

===== [14.2] The bath model Hamiltonian

The Hamiltonian of a system that interact with an environment is conveniently arranged as

$$\mathcal{H}_{\text{total}} = \mathcal{H}_0(x, p) + \mathcal{H}(\mathbf{Q}, \mathbf{P}; x) \quad (633)$$

For an interaction with a general (possibly chaotic) environment we write

$$\mathcal{H}_{\text{total}} = \mathcal{H}_0(x, p) + x\mathbf{B} + \mathbf{E} \quad (634)$$

where $\mathbf{E} = \{E_n\}$ is the bath Hamiltonian that can be written in some diagonal representation, while $\mathbf{B} = \{B_{nm}\}$ represents that interaction term with x . However, it is more conventional to consider an interaction with an harmonic bath:

$$\mathcal{H}_0(x, p) + \mathcal{U}(x, Q_\alpha) + \mathcal{H}_{\text{bath}}(Q_\alpha, P_\alpha) \quad (635)$$

where (say)

$$\mathcal{H}_0(x, p) = \frac{1}{2M} p^2 + V(x) \quad (636)$$

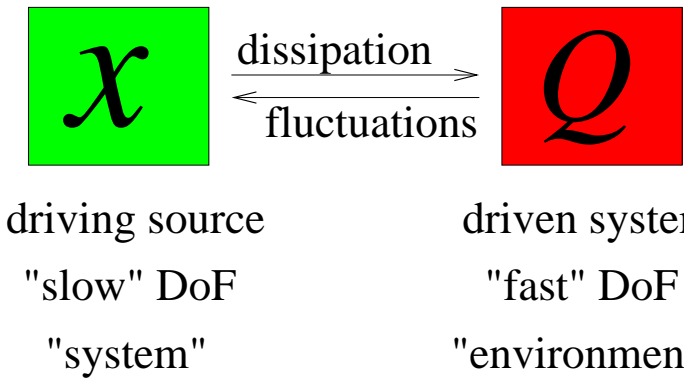
$$\mathcal{H}_{\text{bath}}(Q_\alpha, P_\alpha) = \sum_{\alpha} \left(\frac{P_\alpha^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 Q_\alpha^2 \right) \quad (637)$$

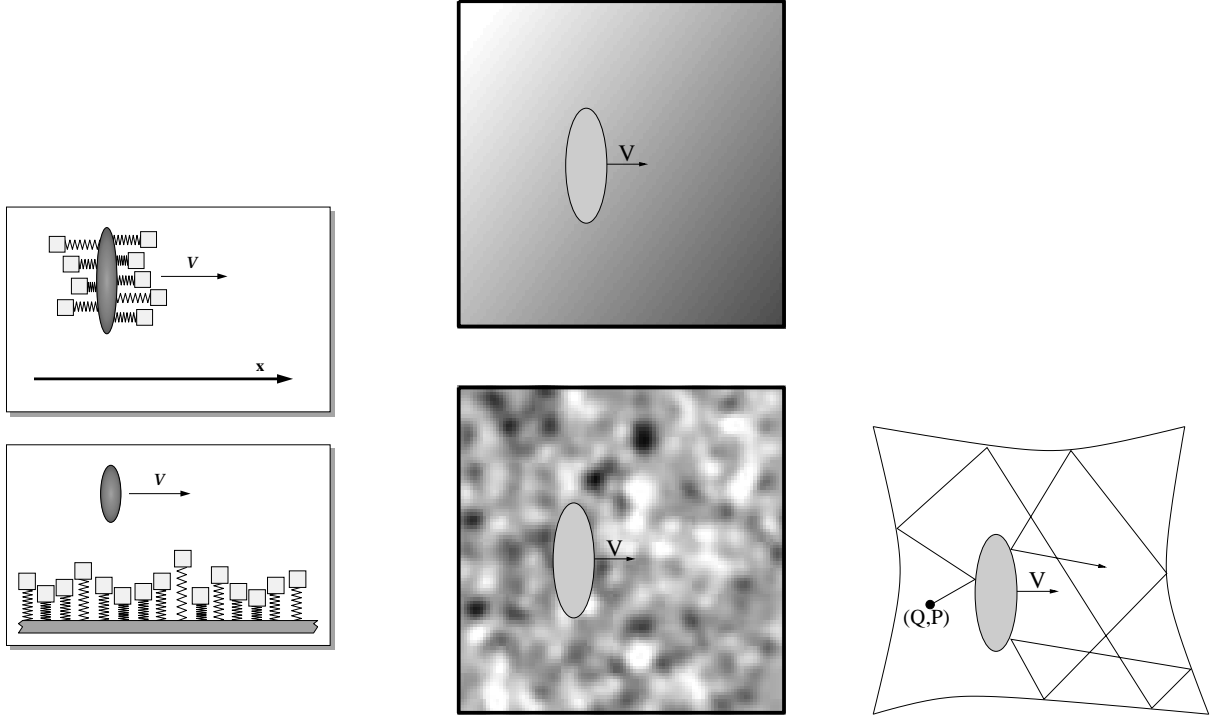
and the interaction is (say)

$$\mathcal{U}_{\text{ZCL}} = -x \sum_{\alpha} c_{\alpha} Q_{\alpha} \quad (638)$$

$$\mathcal{U}_{\text{DLD}} = - \sum_{\alpha} c_{\alpha} Q_{\alpha} u(x - x_{\alpha}) \quad (639)$$

where the DLD possibility is appropriate for the motion of a particle in an extended environment.





==== [14.3] Harmonic bath

It is common to model the environment as a huge collection of harmonic oscillators, and to say that the system is subject to the fluctuations of a field variable \mathcal{F} which is a linear combination of the bath coordinates:

$$\mathcal{F} = \sum_{\alpha} c_{\alpha} Q_{\alpha} = \sum_{\alpha} c_{\alpha} \left(\frac{1}{2m_{\alpha}\omega_{\alpha}} \right)^{1/2} (a_{\alpha} + a_{\alpha}^{\dagger}) \quad (640)$$

For preparation of the bath in state $\mathbf{n} = \{n_{\alpha}\}$ we get

$$\tilde{S}(\omega) = \sum_{\alpha} \sum_{\pm} c_{\alpha}^2 |\langle n_{\alpha} \pm 1 | Q_{\alpha} | n_{\alpha} \rangle|^2 2\pi \delta(\omega \mp \omega_{\alpha}) \quad (641)$$

Using

$$\langle n_{\alpha} + 1 | Q_{\alpha} | n_{\alpha} \rangle = \left(\frac{1}{2m_{\alpha}\omega_{\alpha}} \right)^{1/2} \sqrt{1 + n_{\alpha}} \quad (642)$$

$$\langle n_{\alpha} - 1 | Q_{\alpha} | n_{\alpha} \rangle = \left(\frac{1}{2m_{\alpha}\omega_{\alpha}} \right)^{1/2} \sqrt{n_{\alpha}} \quad (643)$$

we get

$$\tilde{S}(\omega) = \sum_{\alpha} \frac{1}{2m_{\alpha}\omega_{\alpha}} 2\pi c_{\alpha}^2 \left[(1 + n_{\alpha}) \delta(\omega - \omega_{\alpha}) + n_{\alpha} \delta(\omega + \omega_{\alpha}) \right] \quad (644)$$

For a canonical preparation of the bath we have $\langle n_{\alpha} \rangle = f(\omega_{\alpha}) \equiv 1/(e^{\omega/T} - 1)$. It follows that

$$\tilde{S}(\omega) = 2J(|\omega|) \times \begin{cases} (1 + f(\omega)) \\ f(-\omega) \end{cases} = 2J(\omega) \frac{1}{1 - e^{-\beta\hbar\omega}} \quad (645)$$

where we used $f(-\omega) = -(1 + f(\omega))$, and defined the spectral density of the bath as

$$J(\omega) = \frac{\pi}{2} \sum_{\alpha} \frac{c_{\alpha}^2}{m_{\alpha} \omega_{\alpha}} \delta(\omega - \omega_{\alpha}) \quad (646)$$

with anti-symmetric continuation. For an Ohmic bath $J(\omega) = \eta\omega$, with some cutoff frequency ω_c .

===== [14.4] Spin bath

We define \mathcal{F}

$$\mathcal{F} = \sum_{\alpha} c_{\alpha} Q_{\alpha} = \sum_{\alpha} c_{\alpha} (a_{\alpha} + a_{\alpha}^{\dagger}) \quad (647)$$

Thus Q_{α} is the first Pauli matrix. Its non-trivial matrix elements are

$$\langle n_{\alpha}-1 | Q_{\alpha} | n_{\alpha} \rangle = \sqrt{n_{\alpha}} \quad (648)$$

$$\langle n_{\alpha}+1 | Q_{\alpha} | n_{\alpha} \rangle = \sqrt{1 - n_{\alpha}} \quad (649)$$

In complete analogy we get

$$\tilde{S}(\omega) = \sum_{\alpha} 2\pi c_{\alpha}^2 \left[(1 - n_{\alpha}) \delta(\omega - \omega_{\alpha}) + n_{\alpha} \delta(\omega + \omega_{\alpha}) \right] \quad (650)$$

For canonical preparation $\langle n_{\alpha} \rangle = f(\omega_{\alpha})$ where (from here on $\hbar = 1$)

$$f(\omega) = \frac{1}{e^{\beta\omega} + 1} \quad (651)$$

$$f(-\omega) = \frac{1}{1 + e^{-\beta\omega}} = 1 - f(\omega) \quad (652)$$

Thus we get

$$\tilde{S}(\omega) = 2J(|\omega|) \times \begin{cases} (1 - f(\omega)) \\ f(-\omega) \end{cases} = 2J(\omega) \frac{1}{1 + e^{-\beta\omega}} \quad (653)$$

and

$$\tilde{C}(\omega) = J(\omega) \quad (654)$$

where we define

$$J(\omega) = \pi \sum_{\alpha} c_{\alpha}^2 \delta(\omega - \omega_{\alpha}) \quad (655)$$

with symmetric continuation. For Ohmic bath $J(\omega) = \nu$, with some cutoff frequency ω_c .

===== [14.5] Spatially extended environment

In this section we describe fluctuations of an extended environment in space and time using the form factor $\tilde{S}(q, \omega)$. We define

$$\tilde{S}(q, \omega) = \text{FT} \left[\langle \mathcal{U}(x_2, t_2) \mathcal{U}(x_1, t_1) \rangle \right] \quad (656)$$

where the expectation value assumes that the bath is in a stationary state of its unperturbed Hamiltonian. The force-force correlation function is obtained via differentiation. In particular the local power spectrum of the fluctuating force is

$$\tilde{S}(\omega) = \int \frac{dq}{2\pi} q^2 S(q, \omega) \quad (657)$$

and the intensity of the fluctuations at a given point in space is

$$\nu \equiv \tilde{S}(\omega=0) = \int \frac{dq}{2\pi} q^2 S(q, \omega=0) \quad (658)$$

For the one dimensional DLD bath we get

$$\mathcal{U} = - \sum_{\alpha} c_{\alpha} Q_{\alpha} u(x-x_{\alpha}) \quad (659)$$

Taking into account that the oscillators are independent of each other we get

$$\langle \mathcal{U}(x_2, t_2) \mathcal{U}(x_1, t_1) \rangle = \sum_{\alpha} c_{\alpha}^2 \langle Q_{\alpha}(t_2) Q_{\alpha}(t_1) \rangle u(x_2 - x_{\alpha}) u(x_1 - x_{\alpha}) \quad (660)$$

$$= \int dx \left[\sum_{\alpha} c_{\alpha}^2 \langle Q_{\alpha}(t_2) Q_{\alpha}(t_1) \rangle \delta(x - x_{\alpha}) \right] u(x_2 - x) u(x_1 - x) \quad (661)$$

$$= \left[\int u(x_2 - x) u(x_1 - x) dx \right] S(t_2 - t_1) \quad (662)$$

$$= w(x_2 - x_1) S(t_2 - t_1) \quad (663)$$

Where we have assumed homogeneous distribution of the oscillators, and $S(\tau)$ is defined implicitly by the above equality. With the convention $w''(0) = -1$ it is identified as the local force-force correlation function. Consequently we get for the form factor

$$S(q, \omega) = \text{FT} \left[\langle \mathcal{U}(x_2, t_2) \mathcal{U}(x_1, t_1) \rangle \right] = \tilde{w}(q) S(\omega) \quad (664)$$

As an example we may consider the following correlation function:

$$w(r) = \ell^2 \exp \left(-\frac{1}{2} \left(\frac{r}{\ell} \right)^2 \right) \quad (665)$$

If the spatial correlation distance is very large we get ZCL model:

$$w(r) = \text{const} - \frac{1}{2} r^2 \quad (666)$$

leading to

$$S(q, \omega) = \frac{2\pi}{q^2} \delta(q) \tilde{S}(\omega) \quad (667)$$

This means that the force is homogeneous in space, and fluctuates only in time, which is effectively the case if a particle or an atom interacts with long wavelength modes.

[15] Stochastic picture of the dynamics

There are various "levels" in which the dynamics of a non-isolated system can be treated. We start with the random walk problem that can describe the motion of a Brownian particle in the absence of friction. Then we discuss the Langevin equation where friction is included. The dynamics in the above problem is described by a diffusion equation and Fokker-Planck equation respectively. More generally we can talk about Master equations and in particular their simplest stochastic version which is known as rate equations.

===== [15.1] Random walk and diffusion

Consider a particle that can hop from site to site in a stochastic manner. Each step can be represented by a random number $f_t = \pm a$, where a is the lattice constant and t is the integer time index. The total displacement is

$$x(t) - x(0) = \sum_{t'=0}^t f(t') \quad (668)$$

Assuming a stationary stochastic process in which the correlation function is

$$\langle f(t_1)f(t_2) \rangle = C(t_1 - t_2) \quad (669)$$

we get that the variance is

$$\text{Var}[x] = \sum_{t_1=0}^t \sum_{t_2=0}^t \langle f(t_1)f(t_2) \rangle = \sum_{t'=0}^t \sum_{\tau=-t'}^{+t'} C(\tau) \equiv \sum_{t'=0}^t D(t') \longrightarrow 2Dt \quad (670)$$

where the asymptotic value of the diffusion coefficient is

$$D = \frac{1}{2} \sum_{\tau=-\infty}^{\infty} C(\tau) \quad (671)$$

Most significant is to realize that there is a continuum limit of the random walk problem where the dynamics is described by the following "Langevin" equation of motion

$$\dot{x} = f(t) \quad (672)$$

and accordingly

$$D = \frac{1}{2} \int_{-\infty}^{\infty} C(\tau) d\tau = \frac{1}{2} \tilde{C}(\omega=0) \quad (673)$$

There are various generalizations of the random walk problem, where the dwell time or the size of the steps are random variables, leading in general to sub-diffusive or super diffusive behavior respectively. The latter case is known as Levi-flight.

In the random walk problem the stochastic dynamics can be described by an equation for the time evolution of the probabilities p_n to find the particle in site n . This has the form of a "rate equation". In the continuum limit it becomes the "diffusion equation" for the probability density $\rho(x)$ which we describe below. More generally this type of "master equation" is known as the "Fokker Planck equation" which we discuss later on.

===== [15.2] The diffusion equation

It is natural to ask what is the "master equation" that describes the time evolution of the probability density $\rho_t(x)$ in the case of a diffusion process. We assume that the stochastic equation of motion is $\dot{x} = f(t)$ with stochastic $f(t)$ that has a zero average. A trivial generalization is to include a drift term such that the equation is $\dot{x} = u + f(t)$, where u is the so-called drift velocity. In order to derive the diffusion equation, note that for any particular realization of $f(t)$ the probability $\rho_{t+dt}(x_{t+dt})dx_{t+dt}$ must equal $\rho_t(x_t)dx_t$. Since the phase space element preserves its volume one obtains the Liouville equation $(d/dt)\rho_t(x_t) = 0$, from which one deduces the continuity equation

$$\frac{\partial}{\partial t}\rho_t(x) = -(u + f(t)) \frac{\partial \rho_t}{\partial x} \quad (674)$$

From this equation it follows that ρ_{t_0+dt} can be expressed as an integral that involves $\rho_{t'}$ within $t_0 < t' < t_0 + dt$. The equation can be solved iteratively. In order to simplify notations we set without loss of generality $t_0 = 0$ and $t = t_0 + dt$. Consequently we get an expansion that involves nested terms with higher order $\partial/\partial x$ derivatives of ρ_0 . For sake of clarity we drop the drift term and write

$$\rho_t = \rho_0 - \int_0^t dt' f(t') \frac{\partial \rho_0}{\partial x} + \int_0^t dt' f(t') \int_0^{t'} dt'' f(t'') \frac{\partial^2 \rho_0}{\partial x^2} + \text{higher order terms} \quad (675)$$

Averaging over realizations of $f()$, and neglecting the $\mathcal{O}(dt^3)$ terms, one obtains a diffusion equation, to which we add back the drift term:

$$\frac{\partial}{\partial t}\rho = -u \frac{\partial \rho}{\partial x} + D \frac{\partial^2 \rho}{\partial x^2} \quad (676)$$

The neglect of the $\mathcal{O}(dt^3)$ terms is justified in the limit where the correlation time goes to zero. This is sometimes known as the Markovian approximation. It is possible to regard the diffusion equation as a combination of a continuity equation

$$\frac{\partial}{\partial t}\rho_t(x) = -\frac{\partial}{\partial x}I_t(x) \quad (677)$$

with expression to the current that includes a drift term and a diffusion term. The diffusion term is known as Fick's law. The drift velocity is typically related to the gradient of an external potential, $u = -\mu V'(x)$, with a coefficient which is called mobility. Accordingly we write

$$I(x) = u\rho_t(x) - D \frac{\partial}{\partial x}\rho_t(x) = -\mu\rho \frac{\partial V}{\partial x} - D \frac{\partial \rho}{\partial x} \quad (678)$$

If this expression is applied to a system in canonical equilibrium with $\rho(x) \propto \exp(-\beta V(x))$, it follows from the requirement $I(x) = 0$ that $\mu = (1/T)D$. This is called Einstein relation. It is useful in semiconductor physics. For electrons in metal it is common to define the conductivity $\sigma = \mu\rho$, and postulate that at equilibrium $\rho(x) = \int dE g(E - V(x))f(E - E_F)$. It follows that the Einstein relation for metals is $\sigma = g(E_F)D$. Note that $g(E_F)$ is defined here as the density of one-particle states per unit volume, and it is proportional to ρ/E_F .

Fick's law can be explained heuristically as reflecting non-zero net current due to a difference in currents at points $x \pm \ell$, where ℓ is the mean free path. Ignoring the drift, if we have a sample of length L with a steady state current then

$$I = -\frac{D}{L} \times [\rho(L) - \rho(0)] \quad (679)$$

This means that there is a strict analogy here to Ohm law, implying that D is formally like the conductivity of the chain, and accordingly can be obtained from a resistor network calculation. This observation is useful in analyzing diffusion in non-homogeneous networks.

===== [15.3] The Langevin equation

Consider a test particle subject to a homogeneous but fluctuating field of force \mathcal{F} , leading to stochastic dynamics that is described by the Langevin equation $m\ddot{x} = \mathcal{F}$. It is convenient to isolate the average (= “friction”) term from \mathcal{F} , and accordingly to redefine \mathcal{F} as a stochastic variable (= “noise”) that has zero average. Consequently the Langevin equation is written as

$$m\ddot{x} = -\eta\dot{x} + \mathcal{F}(t) \quad (680)$$

where \mathcal{F} is a stochastic variable that satisfies

$$\langle \mathcal{F}(t) \rangle = 0 \quad (681)$$

$$\langle \mathcal{F}(t_2)\mathcal{F}(t_1) \rangle = C(t_2 - t_1) \quad (682)$$

It is assumed that $C(\tau)$ has a short correlation time. We are interested in the dynamics over larger time scales (we have no interest to resolve the dynamics over very short times). We also note that if \mathcal{F} were a constant force, then the particle would drift with velocity $(1/\eta)\mathcal{F}$. The coefficient $\mu = 1/\eta$ is called *mobility*. The equation for the velocity $v = \dot{x}$ can be written as

$$\frac{d}{dt}e^{(\eta/m)t}v(t) = \frac{1}{m}e^{(\eta/m)t}\mathcal{F}(t) \quad (683)$$

leading to the solution

$$v(t) = \frac{1}{m} \int_{-\infty}^t dt' e^{-(\eta/m)(t-t')} \mathcal{F}(t') \quad (684)$$

We see that $\tau_\eta = m/\eta$ is the damping time. After time $\gg \tau_\eta$ the initial velocity is forgotten, hence the lower limit of the integration can be extended to $-\infty$. Evidently the average velocity is zero. We turn now to calculate the velocity-velocity correlation. “Squaring” and averaging over realizations we get

$$\langle v(t_2)v(t_1) \rangle = \frac{1}{m^2} \int_{-\infty}^{t_1} \int_{-\infty}^{t_2} dt' dt'' e^{-(\eta/m)(t_1+t_2-t'-t'')} C(t' - t'') \quad (685)$$

We treat $C(t' - t'')$ like a delta function. Then it is not difficult to find that

$$\langle v(t_2)v(t_1) \rangle = \frac{1}{2\eta m} e^{-(\eta/m)|t_2-t_1|} \int_{-\infty}^{\infty} C(\tau) d\tau = \frac{1}{m} \left(\frac{\nu}{2\eta} \right) e^{-|t_2-t_1|/\tau_\eta} \quad (686)$$

The velocity velocity correlation function should coincide (for $t_1 = t_2 = t$) with the canonical result $\langle \frac{1}{2}mv^2 \rangle = \frac{1}{2}T$. From this one deduces an FD relation $\nu/(2\eta) = T$ with regard to the response characteristics of the bath. The displacement $x(t) - x(0)$ of the particle is the integral over its velocity $v(t')$. On the average it is zero, but the second moment is

$$\langle (x(t) - x(0))^2 \rangle = \int_0^t \int_0^t dt' dt'' \langle v(t'')v(t') \rangle = \frac{\nu}{\eta^2} \times t \equiv 2Dt \quad (687)$$

Hence we have diffusion in space. From the above we deduce the Einstein relation

$$\frac{D}{\mu} = \frac{\nu}{2\eta} = \text{Temperature} \quad (688)$$

The last equality is based on FD relation.

===== [15.4] The Fokker-Planck equation

As in the case of a "random walk" one can ask what is the "master equation" that described the evolution of the probability density $\rho(x, p)$. This leads to the Fokker-Planck equation. The derivation is the same as in the case of a diffusion process. Here the diffusion is in momentum with a coefficient $\nu/2$. Including the $v(p) = p/m$ drift in the position, we get the continuity equation

$$\frac{\partial}{\partial t} \rho = -\frac{\partial}{\partial x} [v\rho] - \frac{\partial}{\partial p} \left[-V'(x)\rho - \eta v\rho - \frac{\nu}{2} \frac{\partial \rho}{\partial p} \right] \quad (689)$$

There are quantum generalizations of the Fokker-Planck equation which we discuss in a separate section.

===== [15.5] Rate equations

A rate equation is merely a discrete version of the diffusion or Fokker-Planck equation. It can be regarded as describing a generalized "random walk" problem, where the transition rates \mathcal{W}_{nm} are not necessarily equal in the $n \mapsto m$ and $m \mapsto n$ directions. In the context of the "system-bath" paradigm it is common to model the system as a set of levels $\{E_n\}$ with transition rates

$$\mathcal{W}_{nm} = w_{nm}^{\varepsilon} + \frac{2w_{nm}^{\beta}}{1 + e^{(E_n - E_m)/T_B}} \quad (690)$$

where w_{nm}^{ε} and w_{nm}^{β} are the elements of symmetric matrices. The first term describes the transitions that are induced by the $T_A = \infty$ driving source, as in the standard random walk problem. The second term describes the bath induced transitions, with ratio $e^{(E_n - E_m)/T_B}$ of $n \leftrightarrow m$ transitions, as required by detailed balance considerations.

One can regard w_{nm}^{β} as the "noise" which is introduced into the system by the bath, while the difference $\mathcal{W}_{nm} - \mathcal{W}_{mn}$ is the friction. However this point of view is strictly correct only for constant density of states. If the level density grows with energy there will be a heating effect even if the $T_B = \infty$.

The dynamics of the population probabilities $\mathbf{p} = \{p_n\}$ is described by a rate equation

$$\frac{dp_n}{dt} = \sum_m [\mathcal{W}_{nm} p_m - \mathcal{W}_{mn} p_n] \quad (691)$$

This equation can be written schematically as $\dot{\mathbf{p}} = \mathcal{W}\mathbf{p}$. There is an implicit conservation of probability requirement $\sum p_n = 1$. The diagonal elements of \mathcal{W} are $-\Gamma_n$, with the decay rates $\Gamma_n = \sum_m \mathcal{W}_{mn}$. The steady state is determined from the matrix equation $\mathcal{W}\mathbf{p} = 0$. In the presence of driving the detailed balance is disturbed leading in general to a non-canonical steady state.

Diffusion.— It is useful to note that a rate equation that describes motion in 1D, with transition rates that depends on the hopping distance, leads to diffusion with a coefficient

$$D = \frac{1}{2} \sum_{r=-\infty}^{\infty} r^2 w(r) \quad (692)$$

In particular for near neighbor hopping $D = w$. Here the distance between the sites is assumed to be unity. If we discretize a diffusion equation by slicing the x axis into cells of width dx , the effective hopping rate w should be chosen such that $D = wdx^2$.

Two level system.— There is an elegant way to write the general rate equation for a two level system. Defining $S_z = p_+ - p_-$, and recalling that $p_+ + p_- = 1$, one realizes that the two equations for \dot{p}_+ and \dot{p}_- can be written as a single equation (whose full quantum version will be discuss in the next lecture):

$$\dot{S}_z = (w_{+-} - w_{-+}) - (w_{+-} + w_{-+})S_z \equiv -\frac{1}{T_1} (S_z - S_{\text{eq}}) \quad (693)$$

[16] Quantum master equations

===== [16.1] General perspective

The description of the reduced dynamics of a system that is coupled to a bath using a Master equation is commonly based on the following working hypothesis: **(i)** The bath is fully characterized by a single spectral function. **(ii)** There is a way to justify the neglect of memory effects. The latter is known as the Markovian approximation. In particular it follows that the initial preparation, whether it is factorized or not, is not an issue. If the master equation is regarded as *exact* description of the reduced dynamics it should be of the Lindblad form. Otherwise it should be regarded merely as an approximation.

There are two common approximation schemes: **(A)** In the *Microscopic regime* of atomic physics (e.g. two level atom) it is assumed that the bath induced rates are much smaller than the level spacing, and a "secular approximation" is employed. **(B)** In the *Mesoscopic regime* of condense matter physics (e.g. Brownian motion) it is assumed that the bath is Ohmic, and accordingly its effect can be treated as a generalization of "white noise".

In the following presentation we assume that the full Hamiltonian is

$$\mathcal{H}_{\text{total}} = \mathcal{H} - WF_{\text{bath}} + \mathcal{H}_{\text{bath}} \quad (694)$$

Neglecting the interaction, the bath is characterized by the spectral function

$$\tilde{C}(\omega) = \text{FT} \left[\langle F(t)F(0) \rangle \right] \quad (695)$$

and the convention $\langle F(t) \rangle = 0$. Whether the bath is composed of harmonic oscillators or not is regarded by the working hypothesis as not important. There is a well known discussion of this point in Feynman-Vernon paper.

The spectral function $\tilde{C}(\omega)$ is characterized by temperature T and by a cutoff frequency ω_c . The latter is assumed below to be large compared with any other temporal frequency. What we call "noise" means $\tilde{C}(-\omega) = \tilde{C}(\omega)$. What we call "finite temperature" means

$$\tilde{C}(-\omega)/\tilde{C}(\omega) = \exp(-\omega/T) \quad (696)$$

What we call "white noise" or "infinite temperature Ohmic bath" corresponds to $\tilde{C}(\omega) = \nu$, leading to

$$C(t) = \langle F(t)F(0) \rangle = \nu \delta(t) \quad (697)$$

What we call "high temperature Ohmic bath" takes into account that $\tilde{C}(\omega)$ possesses an antisymmetric component that at small frequencies can be approximated as $\nu \times [\omega/(2T)]$. Consequently

$$C(t) = \langle F(t)F(0) \rangle = \nu \delta(t) + i\eta \delta'(t) \quad (698)$$

where $\eta = \nu/(2T)$ is the so called friction coefficient.

===== [16.2] Quantum Fokker-Planck equation

The best known of reduced dynamics is known in the classical context as the Langevin equation. Using units such that the mass is unity, and p is the velocity, the stochastic equation is $\dot{p} = -V'(x) - \eta p + f(t)$, where $f(t)$ is white noise. The corresponding master equation for $\rho(x, p)$ is known as the Fokker-Planck equation:

$$\frac{d\rho}{dt} = -\frac{\partial}{\partial x} [p\rho] - \frac{\partial}{\partial p} \left[-V'(x)\rho - \eta p\rho - \frac{\nu}{2} \frac{\partial \rho}{\partial p} \right] \quad (699)$$

This equation can be written with Poisson Brackets $-i[A, B]$ as

$$\frac{d\rho}{dt} = -i[\mathcal{H}, \rho] - \frac{\nu}{2}[x, [x, \rho]] - i\frac{\eta}{2}[x, \{p, \rho\}] \quad (700)$$

The same procedure to eliminate $F(t)$ can be used in the quantum case (see section below), and the same equation is obtained with x replaced by $X = W$ and p replaced by $P = i[\mathcal{H}, W]$

$$\frac{d\rho}{dt} = -i[\mathcal{H}, \rho] - \frac{\nu}{2}[X, [X, \rho]] - i\frac{\eta}{2}[X, \{P, \rho\}] \quad (701)$$

One should notice that this equation is not Lindblad form (see section below). The following term is missing:

$$\text{missing term for Lindblad} = -\frac{\eta^2}{8\nu}[P, [P, \rho]] = -\frac{\eta}{16T}[P, [P, \rho]] \quad (702)$$

The three bath terms of the Fokker-Planck equation can be regarded as an expansion in powers of (Ω/T) , where Ω is the frequency of the motion. Accordingly in the high temperature regime the deviation of Fokker-Planck from Lindblad form is small.

===== [16.3] Derivation for white noise

We demonstrate the derivation of the Master equation in that case of white noise. The Hamiltonian is $\mathcal{H}(t) = \mathcal{H} + f(t)W$, where $f(t)$ represents white noise: that means that upon ensemble average $\langle f(t) \rangle = 0$, while $\langle f(t)f(t') \rangle = \nu\delta(t-t')$. Given $\rho(t) \equiv \rho$, the Liouville von-Neumann equation can be solved iteratively to determine $\rho(t+dt)$, where dt is a small time interval:

$$\rho(t+dt) = \rho - i \int_t^{t+dt} dt' [\mathcal{H}(t'), \rho] - \int_t^{t+dt} \int_t^{t'} dt' dt'' [\mathcal{H}(t'), [\mathcal{H}(t''), \rho]] + \dots \quad (703)$$

Averaging over realizations of $f(t)$ all the odd orders in this expansion vanish, while the leading dt contribution comes only from the zero order term that involves \mathcal{H} and from the second order term that involves W . Consequently we get the following Master equation:

$$\frac{d\rho}{dt} = -i[\mathcal{H}, \rho] - \frac{1}{2}\nu[W, [W, \rho]] = -i[\mathcal{H}, \rho] - \frac{1}{2}\{\Gamma, \rho\} + \nu W\rho W \quad (704)$$

where $\Gamma = \nu WW$. Note that the first two terms in the second expression generate so called non-Hermitian dynamics with the effective Hamiltonian $\mathcal{H}_{\text{eff}} = \mathcal{H} - (i/2)\Gamma$, while the last term represents "continuous measurement".

===== [16.4] Derivation for Ohmic bath

The generalization of the "white noise" derivation for a system that is coupled to a high temperature Ohmic bath is straightforward. It is based on the assumption that at any moment the system-bath state is "factorized", which can be justified if ω_c^{-1} is sufficiently small. Using the same procedure as for "white noise" one obtains:

$$\frac{d\rho}{dt} = -i[\mathcal{H}, \rho] + W^+ \rho W + W \rho W^- - W W^+ \rho - \rho W^- W \quad (705)$$

where

$$W^\pm \equiv \int_0^\infty C(\pm t) W(-t) dt, \quad W(t) \equiv e^{i\mathcal{H}t} W e^{-i\mathcal{H}t} \quad (706)$$

For high temperature Ohmic bath we define $W = X$ and $P = i[\mathcal{H}, X]$ and hence

$$W^\pm = \frac{\nu}{2}X \pm i\frac{\eta}{2}P \quad (707)$$

Consequently we get the Fokker-Planck equation

$$\frac{d\rho}{dt} = -i[\mathcal{H}, \rho] - \frac{\nu}{2}[X, [X, \rho]] - i\frac{\eta}{2}[X, \{P, \rho\}] \quad (708)$$

===== [16.5] Comparison with Lindblad form

A term in the Master equation is of Lindblad form if it can be written as:

$$\text{Lindblad} = \mathbf{W}\rho\mathbf{W}^\dagger - \frac{1}{2}\mathbf{W}^\dagger\mathbf{W}\rho - \frac{1}{2}\rho\mathbf{W}^\dagger\mathbf{W} \quad (709)$$

Writing

$$\mathbf{W} = A + iB \quad (710)$$

$$C = i[A, B] \quad (711)$$

$$D = (1/2)\{A, B\} \quad (712)$$

and using the identity

$$[A, \{B, \rho\}] = \frac{1}{2}[D, \rho] - \frac{i}{2}\{C, \rho\} + A\rho B - B\rho A \quad (713)$$

we get the following optional expressions for the Lindblad term:

$$\text{Lindblad} = -i[D, \rho] - \frac{1}{2}\{A^2 + B^2, \rho\} + A\rho A + B\rho B - i[A, \{B, \rho\}] \quad (714)$$

$$= -i[D, \rho] - \frac{1}{2}[A, [A, \rho]] - \frac{1}{2}[B, [B, \rho]] - i[A, \{B, \rho\}] \quad (715)$$

The first term represents "Lamb shift", the second and the third are "noise" induced diffusion terms, and the last is the "friction" term. Note that the Fokker-Planck equation would be of this form if a positional diffusion term were added.

===== [16.6] The general Lindblad form

A master equation is of Lindblad form if it can be written as

$$\frac{d\rho}{dt} = -i[\mathcal{H}, \rho] + \sum_r [\mathbf{W}^r]\rho[\mathbf{W}^r]^\dagger - \frac{1}{2}[\mathbf{\Gamma}\rho + \rho\mathbf{\Gamma}], \quad \mathbf{\Gamma} = \sum_r [\mathbf{W}^r]^\dagger[\mathbf{W}^r] \quad (716)$$

Lindblad equation is the most general form of a Markovian master Equation for the probability matrix. The heart of the argument is as follows: The most general linear relation between matrices is

$$\tilde{\rho}_{\alpha\beta} = \sum_{\alpha'\beta'} \mathcal{W}(\alpha\beta|\alpha'\beta') \rho_{\alpha'\beta'} \quad (717)$$

This linear transformation is required to preserve the hermiticity of ρ . Changing notation to $\mathcal{W}(\alpha\beta|\alpha'\beta') = \mathcal{W}_{\alpha\alpha',\beta\beta'}$ one observes that $\mathcal{W}_{\alpha\alpha',\beta\beta'}$ should be hermitian, with eigenvalues w_r . Accordingly we can find a spectral decomposition with a transformation matrix $T(\alpha\alpha'|r)$. Changing notation to $\mathbf{W}_{\alpha,\alpha'}^r = \sqrt{w_r}T(\alpha\alpha'|r)$ we get the Lindblad from $\sum_r [\mathbf{W}^r]\rho[\mathbf{W}^r]^\dagger$. Now we have to distinguish between two cases: If $\tilde{\rho}$ is the new probability matrix, then conservation of trace requires $\sum_r [\mathbf{W}^r]^\dagger[\mathbf{W}^r] = \mathbf{1}$. If on the other hand we look on the incremental change $\dot{\rho}$, then (after some non-trivial algebra) we arrive to the Lindblad from of the Master equation. There is a complete analogy here with the Pauli equation where the decay rates in the main diagonal of \mathcal{W} have to counter-balance the ingoing transitions.

===== [16.7] The secular approximation

We start again, as in the Mesoscopic case, with

$$\frac{d\rho}{dt} = -i[\mathcal{H}, \rho] + W^+ \rho W + W \rho W^- - W W^+ \rho - \rho W^- W \quad (718)$$

We can write $W(t)$ as $\sum_{n,m} |n\rangle W_{nm} e^{i(E_n - E_m)t} \langle m|$ or schematically as $\sum_{\Omega} e^{-i\Omega t} A_{\Omega}$. We obtain

$$W^{\pm} = \sum_{\Omega} \tilde{C}^{\pm}(\Omega) A_{\Omega}, \quad \Omega = -(E_n - E_m), \quad A_{\Omega} = |n\rangle W_{nm} \langle m| \quad (719)$$

The secular approximation means that we keep only "resonant terms". For example in $W^+ \rho W$ we keep only the terms $\tilde{C}^+(\Omega) A_{\Omega} \rho A_{\Omega}^\dagger$. Consequently

$$\frac{d\rho}{dt} = -i[\mathcal{H}, \rho] + \sum_{\Omega} \left[(\tilde{C}^+(\Omega) + \tilde{C}^-(\Omega)) A_{\Omega} \rho A_{\Omega}^\dagger - \tilde{C}^+(\Omega) A_{\Omega}^\dagger A_{\Omega} \rho - \tilde{C}^-(\Omega) \rho A_{\Omega}^\dagger A_{\Omega} \right] \quad (720)$$

This approximation will be better explained in the next section. Note that the real part of $\sum_{\pm} \tilde{C}^{\pm}(\Omega)$ is the spectral intensity $\tilde{C}(\Omega)$ that drives the FGR transitions:

$$w_{nm} = (\text{FGR transition rate from } m \text{ to } n) = \tilde{C}(-(E_n - E_m)) \times |W_{nm}|^2 \quad (721)$$

The imaginary part of $\tilde{C}^{\pm}(\Omega)$ determines the Lamb shifts.

===== [16.8] The Pauli Master equation

In atomic physics applications the induced rate of transitions w becomes much smaller compared with the Rabi-Bloch frequency Ω of the coherent oscillations. Then we can ignore all the highly oscillating terms that involve the off-diagonal terms, because they average to zero. Consequently we get the so-called Pauli master equation for the probabilities p_n

$$\frac{d\mathbf{p}}{dt} = \mathcal{W} \mathbf{p}, \quad \mathcal{W} = \begin{pmatrix} -\Gamma_1 & w_{12} & \dots \\ w_{21} & -\Gamma_2 & \dots \\ \dots & \dots & \dots \end{pmatrix} \quad (722)$$

In this equation the \mathcal{W} matrix is in agreement with the FGR picture. Namely, the rate constants are $w_{nm} = \nu |W_{nm}|^2$, and the decay constants are $\Gamma_n = \sum_m w_{nm}$. It is convenient to exclude here the diagonal elements of \mathcal{W} , and to treat them later separately.

If we have an interaction with a bath, then the ratio w_{nm}/w_{mn} is not unity, but would favor downwards transitions.

As for the off-diagonal terms: with the same reasoning we regard the ρ_{nm} as independently oscillating with *different* frequencies, i.e. with negligible cross interaction. Consequently we get

$$\frac{d\rho_{nm}}{dt} = \left[-i(E_n - E_m) - \gamma_{nm} \right] \rho_{nm}, \quad \gamma_{nm} = \frac{1}{2}(\Gamma_n + \Gamma_m) + \frac{\nu}{2}|W_{nn} - W_{mm}|^2 \quad (723)$$

===== [16.9] The Bloch equation (NMR)

Taking a two level system as an example, and adopting the NMR spin language, the Pauli equation takes the form of a Bloch equation for the so-called polarization or Bloch vector (S_x, S_y, S_z) . Note that $S_z = p_+ - p_-$ is the population probability difference. The Bloch equations are:

$$\frac{dS_z}{dt} = -\frac{1}{T_1}(S_z - S_{\text{eq}}) \quad (724)$$

$$\frac{dS_{x,y}}{dt} = -[\Omega \times S]_{x,y} - \frac{1}{T_2} S_{x,y} \quad (725)$$

where $S_{\text{eq}} = (w_{+-} - w_{-+})/(w_{+-} + w_{-+})$. The rates for the diagonal relaxation and for the off-diagonal transverse dephasing are:

$$\frac{1}{T_1} = w_{+-} + w_{-+} \equiv 2w \quad (726)$$

$$\frac{1}{T_2} = \frac{1}{2}(w_{+-} + w_{-+}) + \gamma_\varphi \equiv \gamma \quad (727)$$

The pure dephasing rate γ_φ originated from the diagonal elements of W_{nm} and hence is formally proportional to $\tilde{C}(0)$, while the FGR transition rates originate from the off-diagonal elements of W_{nm} , and hence are proportional to $\tilde{C}(\pm\Omega)$, where $\Omega = |E_+ - E_-|$ is the level spacing. Note that the transverse components satisfy the equation

$$\ddot{S} + \gamma\dot{S} + \Omega^2 S = 0 \quad (728)$$

which leads to damped frequency $\Omega_{\text{eff}} = \sqrt{\Omega^2 - (\gamma/2)^2}$.

Additional topics

[17] The kinetic picture

===== [17.1] The Boltzmann distribution function

The number of one particle states within a phase space volume is $d\mathcal{N} = d^3r d^3p / (2\pi\hbar)^3$. The occupation of this phase space volume is:

$$dN \equiv f(\mathbf{r}, \mathbf{p}) \frac{d\mathbf{r} d\mathbf{p}}{(2\pi\hbar)^3} \quad (729)$$

where $f(\mathbf{r}, \mathbf{p})$ is called Boltzmann distribution function. In equilibrium we have

$$f(\mathbf{r}, \mathbf{p}) \Big|_{\text{eq}} = f(\epsilon_{\mathbf{p}} - \mu) \quad (730)$$

where $f(\epsilon - \mu)$ is either the Bose or the Fermi occupation function, or possibly their Boltzmann approximation. If we use (\mathbf{r}, \mathbf{v}) with measure $d^3r d^3v$ instead of (\mathbf{r}, \mathbf{p}) we have

$$f(\mathbf{r}, \mathbf{v}) = \left(\frac{m}{2\pi}\right)^3 f(\mathbf{r}, \mathbf{p}) \quad (731)$$

By integrating over \mathbf{r} and over all directions we get the velocity distribution

$$F(v) = L^3 \times 4\pi v^2 \left(\frac{m}{2\pi}\right)^3 f\left(\frac{1}{2}mv^2 - \mu\right) \quad (732)$$

If we use Boltzmann approximation for the occupation function and express μ using N and T we get

$$F(v) = N \left(\frac{m}{2\pi T}\right)^{3/2} 4\pi v^2 e^{-\frac{1}{2}mv^2/T} \quad (733)$$

We note that

$$N = \iint \frac{d\mathbf{r} d\mathbf{p}}{(2\pi\hbar)^3} f(\mathbf{r}, \mathbf{p}) = \int d\epsilon g(\epsilon) f(\epsilon - \mu) = \int F(v) dv \quad (734)$$

===== [17.2] The Boltzmann equation

The Liouville equation for $\rho(r, p)$ is merely a continuity equation in phase space. It can be written as $(d/dt)\rho = 0$ where d/dt unlike $\partial/\partial t$ is the total derivative reflecting the change in the occupation of a phase space cell. The Boltzmann equation for $f(r, p)$ is formally identical to the Liouville equation in the absence of collisions, and with collisions becomes $(d/dt)\rho = g(r, p)$, where $g(r, p)$ is the net rate in which particles are generated at (r, p) due to collisions. Accordingly the Boltzmann equation is

$$\left[\frac{\partial}{\partial t} + v(p) \cdot \frac{\partial}{\partial x} + \mathcal{F}(r) \cdot \frac{\partial}{\partial p} \right] f(r, p) = g(r, p) \quad (735)$$

where $v(p) = p/m$ is the dispersion relation, and $\mathcal{F}(r) = -V'(r)$ is the force due to some external potential. The common expression for $g(r, p)$ is based on 2body collision mechanism and "molecular chaos" assumption. The gas

reaches a steady state in accordance with the Boltzmann H theorem. The formal solution for the steady state implies the Maxwell-Boltzmann distribution for the velocities.

===== [17.3] The calculation of incident flux

Given N gas particles that all have velocity v we can calculate the number of particles that hit a wall element per unit time (=flux), and also we can calculate the momentum transfer per unit time (=force). Using spherical coordinates, such that normal incidence is $\theta=0$, one obtains (per unit area):

$$J = \iint_{|\theta| < \pi/2} \left[\frac{d\Omega}{4\pi} \frac{N}{V} \right] v \cos(\theta) = \left[\frac{1}{2} \int_0^1 \cos(\theta) d\cos(\theta) \right] \frac{N}{V} v = \frac{1}{4} \left(\frac{N}{V} \right) v \quad (736)$$

$$P = \iint_{|\theta| < \pi/2} \left[\frac{d\Omega}{4\pi} \frac{N}{V} \right] v \cos(\theta) 2mv = \left[\int_0^1 \cos^2(\theta) d\cos(\theta) \right] \frac{N}{V} mv^2 = \frac{1}{3} \left(\frac{N}{V} \right) mv^2 \quad (737)$$

If we have the distribution $F(v)$ of the velocities, or optionally if we are provided with the one-particle energy distribution, the total flux is given by an integral:

$$J_{\text{incident}} = \int_0^\infty \frac{1}{4} \left(\frac{F(v)dv}{V} \right) v = \int_0^\infty \frac{1}{4} \left(\frac{g(\epsilon)f(\epsilon)d\epsilon}{V} \right) v_\epsilon \quad (738)$$

Similar expression holds for the pressure P , where one can make the identification $\epsilon = (1/2)mv_\epsilon^2$, and recover the familiar Grand canonical result.

===== [17.4] Blackbody radiation

The modes of the electromagnetic field are labeled by the wavenumber k and the polarization α . For historical reasons we use k instead of p for the momentum and ω instead of ϵ for the energy. The dispersion relation is linear $\omega = c|k|$. The density of modes is

$$g(\omega)d\omega = 2 \times \frac{V}{(2\pi c)^3} 4\pi\omega^2 d\omega \quad (739)$$

Recall that the canonical state of oscillators can be formally regarded as the grand canonical equilibrium of $\mu = 0$ Bose particles, with the occupation function

$$\langle n_{k\alpha} \rangle = \frac{1}{e^{\beta\omega_{k\alpha}} - 1} \equiv f(\omega_{k\alpha}) \quad (740)$$

For the total energy E we have

$$E = \int_0^\infty \omega d\omega g(\omega) f(\omega) = V \int_0^\infty d\omega \frac{1}{\pi^2 c^3} \left(\frac{\omega^3}{e^{\beta\omega} - 1} \right) \quad (741)$$

For the total number of photons N we have a similar integral but without the ω . The flux of photons is obtained from the formula $J = (1/4)(N/V)c$. From historical perspective we are interested in the flux of energy:

$$J_{\text{incident}}[\text{energy}] = \frac{1}{4} \left(\frac{E}{V} \right) c = \int_0^\infty d\omega \left[\frac{1}{4\pi^2 c^2} \left(\frac{\omega^3}{e^{\beta\omega} - 1} \right) \right] \quad (742)$$

Considering the thermal equilibrium between blackbody radiation from the environment, and the an object with a given temperature, detailed balance consideration implies that

$$J_{\text{emitted}}(\omega) d\omega = a(\omega) J_{\text{incident}}(\omega) d\omega \quad (743)$$

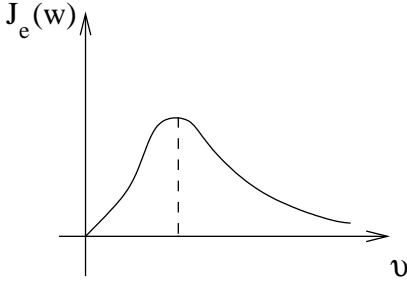
where the emissivity $a(\omega)$ should equal the absorption coefficient of the incident radiation. From here we get the Planck formula

$$J_{\text{emitted}}(\omega) = a(\omega) \frac{1}{4\pi^2 c^2} \left(\frac{\omega^3}{e^{\beta\omega} - 1} \right) = \frac{a(\omega)}{4\pi^2 c^2} T^3 \left(\frac{\nu^3}{e^\nu - 1} \right) \quad (744)$$

where $\nu = \omega/T$ is the scaled frequency. Note that the peak of a blackbody radiation is at $\nu \approx 3$ which is known as Wein's law. Upon integration the total blackbody radiation is

$$J_{\text{emitted}} = \int_0^\infty J_{\text{emitted}}(\omega) d\omega = \frac{1}{4\pi^2 c^2} \left(\frac{\pi^4}{15} \right) T^4 \quad (745)$$

which is known as Stephan-Boltzmann Law. Note that the units of the flux are energy per time per unit area.



===== [17.5] Viscosity

We have considered above the rate in which momentum is transferred to a wall due to *ballistic* collisions, leading to pressure. There is a somewhat related effect that is called "viscosity". It is simplest to explain the concept with regard to a gas whose particles have a short mean free path ℓ , such that in equilibrium each gas particle has a diffusion coefficient $D = v_T \ell$, where v_T is the mean thermal velocity.

Assume out of equilibrium steady state in which the average velocity of the gas particles $v(x, y, z)$ is in the x direction but its magnitude varies in the y direction. Due to the transverse diffusion there will be momentum transfer across the $y = 0$ plane, which implies that the "upper" flow exerts a force on the "lower" region of the fluid (which is possibly the boundary layer of some "wall"). We shall explain below that if the area of the boundary region is A , then the force on it is given by the "stress-shear equation"

$$F_x = \mu A \frac{dv_x}{dy} \quad (746)$$

where $\mu = \rho D$ is the viscosity, and ρ is the mass density of the gas. The argument goes as follows: Divide the y axis into layers of width dy . Define w , the effective transition rate of particles between layers, such that $D = w dy^2$. Define the flow of momentum between layers as $J(y) = [(\rho dy) v_x(y)] \times w$. Hence $J(dy/2) - J(-dy/2)$ is the rate in which momentum is transferred across $y = 0$, leading to the desired result.

The viscosity plays a major role in the NavierStokes equations. These equations describe the rate of change of the velocity field of a fluid due to momentum transfer. The equation included "pressure" term "viscosity" term and an optional external "force" term (say gravitation). Usually the equation is supplemented by a continuity equations for the mass, and for the energy, as well as by state equation that connects the pressure to the density. A well known result is Stokes law for the friction force that is exerted on a spherical object of radius R

$$F = -6\pi\mu R v_{\text{sphere}} \quad (747)$$

Note the the result depends on the radius and not on the area of the sphere. It holds for incompressible flow with very small Reynolds number. The simplest way to derive it, is to find the velocity field for a potential flow, as if there is no viscosity, but with no-slip boundary conditions, and then to use the "stress-shear equation".

[18] Scattering approach to mesoscopic transport

The most popular approach to transport in mesoscopic devices takes the scattering formalism rather than the Kubo formalism as a starting point, leading to the Landauer and the BPT formulas. We first cite these formulas and then summarize their common derivation. This should be compared with the Kubo-based derivation of the previous section.

===== [18.1] The Buttiker-Pretre-Thomas-Landauer formula

We assume without loss of generality that there are three parameters (x_1, x_2, x_3) over which we have external control, where $x_3 = \Phi$ is the AB flux. The expression for the current \mathcal{I}_A that goes *out* of lead A , assuming DC linear response, can be written as

$$I_A = - \sum_j \mathbf{G}^{3j} \dot{x}_j \quad (748)$$

where $-\dot{x}_3 = -\dot{\Phi}$ is the EMF, and therefore \mathbf{G}^{33} is the conductance in the usual sense. The Büttiker-Prêtre-Thomas-Landauer formula for the generalized conductance matrix is

$$\mathbf{G}^{3j} = \frac{e}{2\pi i} \text{trace} \left(P_A \frac{\partial S}{\partial x_j} S^\dagger \right) \quad (749)$$

In particular for the Ohmic conductance we get the Landauer formula:

$$\mathbf{G}^{33} = \frac{e^2}{2\pi\hbar} \text{trace}(\mathbf{t}\mathbf{t}^\dagger) \quad (750)$$

In order to explain the notations in the above formulas we consider a two lead system. The S matrix in block form is written as follows:

$$S = \begin{pmatrix} \mathbf{r}_B & \mathbf{t}_{AB} e^{-i\phi} \\ \mathbf{t}_{BA} e^{i\phi} & \mathbf{r}_A \end{pmatrix} \quad (751)$$

where \mathbf{r} and \mathbf{t} are the so called reflection and transmission (sub) matrices respectively. We use the notation $\phi = e\Phi/\hbar$. In the same representation, we define the left lead and the right lead projectors:

$$P_A = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}, \quad P_B = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \quad (752)$$

The following identity is important in order to obtain the Landauer formula from the BPT formula:

$$\frac{dS}{d\Phi} = i \frac{e}{\hbar} (P_A S P_B - i P_B S P_A) = i \frac{e}{\hbar} (P_A S - S P_A) = -i \frac{e}{\hbar} (P_B S - S P_B) \quad (753)$$

Another important identity is

$$\text{trace}(P_A S P_B S^\dagger) = \text{trace}(\mathbf{t}\mathbf{t}^\dagger) = \sum_{a \in A} \sum_{b \in B} |\mathbf{t}_{ab}|^2 \quad (754)$$

The $\text{trace}()$ operation is over the channel indexes.

===== [18.2] Floque theory for periodically driven systems

The solution of the Schrodinger equation

$$i \frac{d\psi}{dt} = \mathcal{H}\psi \quad (755)$$

with time independent \mathcal{H} is

$$|\psi(t)\rangle = \sum_{\mathcal{E}} e^{-i\mathcal{E}t} |\psi^{(\mathcal{E})}\rangle \quad (756)$$

where the stationary states are found from

$$\mathcal{H}|\psi^{(\mathcal{E})}\rangle = \mathcal{E}|\psi^{(\mathcal{E})}\rangle \quad (757)$$

Consider now the more complicated case where \mathcal{H} depends periodically on time. Given that the basic frequency is ω we can write

$$\mathcal{H}(t) = \sum \mathcal{H}^{(n)} e^{-in\omega t} \quad (758)$$

The solution of the Schrodinger equation is

$$|\psi(t)\rangle = \sum_{\mathcal{E}} \sum_{n=-\infty}^{\infty} e^{-i(\mathcal{E}+n\omega)t} |\psi^{(\mathcal{E},n)}\rangle \quad (759)$$

where the Floque states are found from

$$\sum_{n'} \mathcal{H}^{(n-n')} |\psi^{(\mathcal{E},n')}\rangle = (\mathcal{E} + n\omega) |\psi^{(\mathcal{E},n)}\rangle \quad (760)$$

and \mathcal{E} is defined modulo ω .

===== [18.3] The Floque scattering matrix

In scattering theory we can define a Floque energy shell \mathcal{E} . The solution outside of the scattering region is written as

$$|\psi(t)\rangle = \sum_{n=n_{\text{floor}}}^{\infty} e^{-i(\mathcal{E}+n\omega)t} \sum_a \left[A_{an} \frac{1}{\sqrt{v_{an}}} e^{-ik_{an}r} - B_{an} \frac{1}{\sqrt{v_{an}}} e^{+ik_{an}r} \right] \otimes |a\rangle \quad (761)$$

where v_{an} and k_{an} are determined by the available energy $\mathcal{E} + n\omega$. The current in a given channel is time dependent, but its DC component is simply $\sum_n (|B_{an}|^2 - |A_{an}|^2)$. Therefore the continuity of the probability flow implies that we can define an on-shell scattering matrix

$$B_{bn_b} = \sum_{an_a} S_{bn_b, an_a} A_{an_a} \quad (762)$$

We can write this matrix using the following notation

$$S_{bn_b, an_a} \equiv S_{b,a}^{n_b - n_a}(\mathcal{E} + n_a\omega) \quad (763)$$

Unitarity implies that

$$\sum_{bn_b} |\mathcal{S}_{bn_b, an_a}|^2 = \sum_{bn} |\mathcal{S}_{b,a}^n(\mathcal{E})|^2 = 1 \quad (764)$$

$$\sum_{an_a} |\mathcal{S}_{bn_b, an_a}|^2 = \sum_{an} |\mathcal{S}_{b,a}^n(\mathcal{E} + n\omega)|^2 = 1 \quad (765)$$

If the driving is very slow we can use the adiabatic relation between the incoming and outgoing amplitudes

$$B_b(t) = \sum_a \mathcal{S}_{ba}(X(t)) A_a(t) \quad (766)$$

where $\mathcal{S}_{ba}(X)$ is the conventional on-shell scattering matrix of the time independent problem. This relation implies that

$$\mathcal{S}_{b,a}^n(\mathcal{E}) = \frac{\omega}{2\pi} \int_0^{\omega/2\pi} \mathcal{S}_{ba}(X(t)) e^{in\omega t} dt \quad (767)$$

For sake of later use we note the following identity

$$\sum_n n |\mathcal{S}_{b,a}^n|^2 = \frac{i}{2\pi} \int_0^{2\pi/\omega} dt \frac{\mathcal{S}_{ba}(X(t))}{\partial t} \mathcal{S}_{ba}(X(t)) \quad (768)$$

===== [18.4] Current within a channel

Consider a one dimensional channel labeled as a . Let us take a segment of length L . For simplicity assume periodic boundary condition (ring geometry). If one state n is occupied the current is

$$I_{a,n} = \frac{e}{L} v_{a,n} \quad (769)$$

If several states are occupied we should integrate over the energy

$$I_a = \sum_n f_a(E_n) I_{a,n} = \int f_a(E) \frac{L dE}{2\pi v_a} \left(\frac{e}{L} v_a \right) = \frac{e}{2\pi} \int f_a(E) dE \quad (770)$$

For fully occupied states withing some energy range we get

$$I_a = \frac{e}{2\pi} (E_2 - E_1) = \frac{e^2}{2\pi} (V_2 - V_1) \quad (771)$$

If we have a multi channel lead, then we have to multiply by the number of open channels.

===== [18.5] The Landauer formula

Consider a multi channel system which. All the channels are connected to a scattering region which is described by an \mathcal{S} matrix. We use the notation

$$g_{ba} = |\mathcal{S}_{ba}|^2 \quad (772)$$

Assuming that we occupy a set of scattering states, such that $f_a(E)$ is the occupation of those scattering states that incident in the a th channel, we get that the outgoing current at channel b is

$$I_b = \frac{e}{2\pi} \int dE \left[\left(\sum_a g_{ba} f_a(E) \right) - f_b(E) \right] \quad (773)$$

Inserting $1 = \sum_a g_{ba}$ in the second term we get

$$I_b = \frac{e}{2\pi} \int dE \left[\sum_a g_{ba} (f_a(E) - f_b(E)) \right] \quad (774)$$

Assuming low temperature occupation with

$$f_a(E) = f(E - eV_a) \approx f(E) - f'(E)eV_a \quad (775)$$

we get

$$I_b = -\frac{e^2}{2\pi} \sum_a g_{ba} (V_b - V_a) \quad (776)$$

which is the multi channel version of the Landauer formula. If we have two leads A and B we can write

$$I_B = -\frac{e^2}{2\pi} \left[\sum_{b \in B} \sum_{a \in A} g_{ba} \right] (V_B - V_A) \quad (777)$$

Form here it follows that the conductance is

$$G = \frac{e^2}{2\pi} \sum_{b \in B} \sum_{a \in A} g_{ba} = \frac{e^2}{2\pi} \text{trace}(P_B \mathbf{S} P_A \mathbf{S}^\dagger) \quad (778)$$

where P_A and P_B are the projectors that define the two leads.

===== [18.6] The BPT formula

Assuming that the scattering region is periodically driven we can use the Floque scattering formalism. The derivation of the expression for the DC component I_b of the current in channel b is very similar to the Landauer case, leading to

$$I_b = \frac{e}{2\pi} \int dE \left[\left(\sum_{a,n} |\mathbf{S}_{ba}^n(E - n\omega)|^2 f_a(E + n\omega) \right) - f_b(E) \right] \quad (779)$$

$$= \frac{e}{2\pi} \int dE \left[\sum_{a,n} |\mathbf{S}_{ba}^n(E - n\omega)|^2 (f_a(E - n\omega) - f_b(E)) \right] \quad (780)$$

$$= \frac{e}{2\pi} \int dE \left[\sum_{a,n} |\mathbf{S}_{ba}^n(E)|^2 (f_a(E) - f_b(E + n\omega)) \right] \quad (781)$$

$$\approx \frac{e}{2\pi} \int dE \left[\sum_{a,n} n\omega |\mathbf{S}_{ba}^n(E)|^2 (-f'_a(E)) \right] = \frac{e}{2\pi} \left[\sum_{a,n} n\omega |\mathbf{S}_{ba}^n(E)|^2 \right] \quad (782)$$

In the last two steps we have assumed very small ω and zero temperature Fermi occupation. Next we use an identity that has been mentioned previously in order to get an expression that involves the time independent scattering matrix:

$$I_b = i \frac{e}{2\pi} \sum_a \frac{\omega}{2\pi} \int_0^{2\pi/\omega} dt \frac{\mathbf{S}_{ba}(X(t))}{\partial t} \mathbf{S}_{ba}(X(t)) \quad (783)$$

which implies that the pumped charge per cycle is

$$Q = i \frac{e}{2\pi} \oint dX \sum_{b \in B} \sum_a \frac{\mathbf{S}_{ba}(X)}{\partial X} \mathbf{S}_{ba}(X) \equiv - \oint G(X) dX \quad (784)$$

with

$$G(X) = -i \frac{e}{2\pi} \sum_{b \in B} \sum_a \frac{\mathbf{S}_{ba}(X)}{\partial X} \mathbf{S}_{ba}(X) = -i \frac{e}{2\pi} \text{trace} \left(P_B \frac{\partial \mathbf{S}}{\partial X} \mathbf{S}^\dagger \right) \quad (785)$$

Note: since $\mathbf{S}(X)$ is unitary it follows that the following generator is Hermitian

$$\mathbf{H}(X) = i \frac{\partial \mathbf{S}}{\partial X} \mathbf{S}^\dagger \quad (786)$$

The trace of a product of two hermitian operators is always a real quantity.

===== [18.7] BPT and the Friedel sum rule

If only one lead is involved the BPT formula becomes

$$dN = -i \frac{1}{2\pi} \text{trace} \left(\frac{\partial \mathbf{S}}{\partial X} \mathbf{S}^\dagger \right) dX \quad (787)$$

where dN is the number of particles that are absorbed (rather than emitted) by the scattering region due to change dX in some control parameter. A similar formula known as the Friedel sum rule states that

$$d\mathcal{N} = -i \frac{1}{2\pi} \text{trace} \left(\frac{\partial \mathbf{S}}{\partial E} \mathbf{S}^\dagger \right) dE \quad (788)$$

where $\mathcal{N}(E)$ counts the number of states inside the scattering region up to energy E . Both formulas have a very simple derivation, since they merely involve counting of states. For the purpose of this derivation we close the lead at $r = 0$ with Dirichlet boundary conditions. The eigen-energies are found via the equation

$$\det(\mathbf{S}(E, X) - \mathbf{1}) = 0 \quad (789)$$

Let us denote the eigenphases of \mathbf{S} as θ_r . We have the identity

$$i \sum_r \delta \theta_r = \delta [\ln \det \mathbf{S}] = \text{trace}[\delta \ln \mathbf{S}] = \text{trace}[\delta \mathbf{S} \mathbf{S}^\dagger] \quad (790)$$

Observing that a new eigenvalue is found each time that one of the eigenphases goes via $\theta = 0$ we get the desired result.

[19] The theory of electrical conductance

===== [19.1] The Hall conductance

The calculation of the Hall conductance is possibly the simplest non-trivial example for adiabatic non-dissipative response. The standard geometry is a 2D "hall bar" of dimension $L_x \times L_y$. In "Lecture notes in quantum mechanics" we have considered what happens if the electrons are confined in the transverse direction by a potential $V(y)$. Adopting the Landauer approach it is assumed that the edges are connected to leads that maintain a chemical potential difference. Consequently there is a net current in the x direction. From the "Landau level" picture it is clear that the Hall conductance G_{xy} is quantized in units $e^2/(2\pi\hbar)$. The problem with this approach is that the more complicated case of disorder $V(x, y)$ is difficult for handling. We therefore turn to describe a formal Kubo approach. From now on we use units such that $e = \hbar = 1$.

We still consider a Hall bar $L_x \times L_y$, but now we impose periodic boundary condition such that $\psi(L_x, y) = e^{i\phi_x}\psi(0, y)$ and $\psi(x, L_y) = e^{i\phi_y}\psi(x, 0)$. Accordingly the Hamiltonian depends on the parameters (ϕ_x, ϕ_y, Φ_B) , where Φ_B is the uniform magnetic flux through the Hall bar in the z direction. The currents $I_x = (e/L_x)v_x$ and $I_y = (e/L_y)v_y$ are conjugate to ϕ_x and ϕ_y . We consider the linear response relation $I_y = -G_{yx}\dot{\phi}_x$. This relation can be written as $dQ_y = -G_{yx}d\phi_x$. The Hall conductance quantization means that a 2π variation of ϕ_x leads to one particle transported in the y direction. The physical picture is very clear in the standard $V(y)$ geometry: the net effect is to displace all the filled Landau level "one step" in the y direction.

We now proceed with a formal analysis to show that the Hall conductance is quantized for general $V(x, y)$ potential. We can define a "vector potential" A_n on the (ϕ_x, ϕ_y) manifold. If we performed an adiabatic cycle the Berry phase would be a line integral over A_n . By Stokes theorem this can be converted into a $d\phi_x d\phi_y$ integral over B_n . However there are two complementary domains over which the surface integral can be done. Consistency requires that the result for the Berry phase would come out the same modulo 2π . It follows that

$$\frac{1}{2\pi} \int_0^{2\pi} \int_0^{2\pi} B_n d\phi_x d\phi_y = \text{integer} \quad [\text{Chern number}] \quad (791)$$

This means that the ϕ averaged B_n is quantized in units of $1/(2\pi)$. If we fill several levels the Hall conductance is the sum $\sum_n B_n$ over the occupied levels, namely

$$G_{yx} = \sum_{n \in \text{band}} \sum_m \frac{2\text{Im}[I_{nm}^y I_{mn}^x]}{(E_m - E_n)^2} \quad (792)$$

If we have a quasi-continuum it is allowed to average this expression over (ϕ_x, ϕ_y) . Then we deduce that the Hall conductance of a filled band is quantized. The result is of physical relevance if non-adiabatic transitions over the gap can be neglected.

===== [19.2] The Drude formula

The traditional derivation of the Drude formula is based on the Boltzmann picture. Optionally one can adopt a Langevine-like picture. The effect of the scattering of an electron in a metal is to randomize its velocity. This randomization leads to a statistical "damping" of the average velocity with rate $1/t_\ell$. On the other hand the electric field accelerates the particle with rate $e\mathcal{E}/m$. In steady state the drift velocity is $v_{drift} = (e\mathcal{E}/m)t_\ell$, and the current density is $J = (N/V)ev_{drift}$ leading to the Drude conductivity $\sigma = (N/V)(e^2/m)t_\ell$. Consequently the conductance of a ring that has a length L and a cross-section A is

$$G = \frac{A}{L}\sigma = \frac{N}{L^2} \left(\frac{e^2}{m} \right) t_\ell = e^2 \left(\frac{N}{mv_F L} \right) \frac{\ell}{L} \equiv \frac{e^2}{2\pi\hbar} \mathcal{M} \frac{\ell}{L} \quad (793)$$

where $\ell = v_F t_\ell$ is the mean free path at the Fermi energy, and \mathcal{M} is the effective number of open modes. Below we would like to derive this result formally from the FD relation.

The canonical version of the FD relation takes the form $G = [1/(2T)]\nu_T$, where ν is the intensity of the current fluctuations and G is the conductance. This is known as Nyquist version of the FD relation. One way to go is to calculate ν_T for a many body electronic system, see how this is done in a previous lecture. But if the electrons are non-interacting it is possible to do a shortcut, relating the conductance of the non-interacting many body electronic system to its single particle fluctuations. This can be regarded as a generalizations of the canonical Nyquist formula. The generalization is obtained by re-interpretation of $f(E)$ as the Fermi occupation function (with total occupation N), rather than probability distribution. Assuming a Boltzmann occupation one obtains $G^{[N]} = [N/(2T)]\nu_T$. A similar generalization holds for a microcanonical occupation, from which one can deduce results for other occupations. In particular for low temperature Fermi occupation of non-interacting particles one obtains:

$$G^{[N]} = \frac{1}{2}g(E_F) \nu_{E_F} = \frac{1}{2}g(E_F) \left(\frac{e}{L}\right)^2 \int \langle v_{\parallel}(t)v_{\parallel}(0) \rangle dt = \left(\frac{e}{L}\right)^2 g(E_F) \mathcal{D}_0 \quad (794)$$

The crossover from the high temperature "Boltzmann" to the low temperature "Fermi" behavior happens at $T \sim E_F$. Assuming exponential velocity-velocity correlation function with time constant τ_0 , such that the mean free path is $\ell = v_F \tau_0$, we get $\mathcal{D}_0 = v_F \ell$. disregarding numerical prefactors the density of states can be written as $g(E_F) = (L/v_F)\mathcal{M}$, where \mathcal{M} is the number of open modes. From here we get the Drude formula

$$G^{[N]} = \left(\frac{e}{L}\right)^2 g(E_F) \mathcal{D}_0 = \frac{e^2}{2\pi\hbar} \mathcal{M} \frac{\ell}{L} \quad (795)$$

Relating to electrons that are moving in a lattice with static disorder, the mean free path can be deduced from the Fermi Golden Rule (FGR) picture as follows: Assuming isotropic scattering, the velocity-velocity correlation function is proportional to the survival probability $P(t) = e^{-t/t_\ell}$. Ignoring a factor that has to do with the dimensionality $d = 2, 3$ of the sample the relation is

$$\langle v(t)v(0) \rangle \approx v_E^2 P(t) = v_E^2 e^{-|t|/t_\ell} \quad (796)$$

where the FGR rate of the scattering is

$$\frac{1}{t_\ell} = 2\pi \varrho_E |U_{mn}|^2 = \frac{\pi a}{v_E} W^2 \quad (797)$$

In the last equality we have used $|U_{nm}|^2 \approx [a/(\mathcal{M}L)]W^2$, where a is the lattice spacing, and W is the strength of the disorder. Disregarding prefactors of order unity we deduce the so-called Born approximation for the mean free path:

$$\ell = v_E t_\ell \approx \frac{1}{a} \left(\frac{v_E}{W}\right)^2 \quad (798)$$

===== [19.3] Formal calculation of the conductance

The DC conductance G of a ring with N non-interacting electrons is related by Kubo/FD expression to the density of one-particle states $g(E_F)$ at the Fermi energy, and to the $\tilde{C}_{vv}(\omega \sim 0)$ fluctuations of velocity. The latter can be deduced semi-classically from the velocity-velocity correlation function, or from the matrix elements of the velocity operator using the quantum-mechanical spectral decomposition. Optionally one can use path integral or Green function diagrammatic methods for the calculation.

Let us summarize some optional ways in which the Kubo/FD expression for the Ohmic conductance can be written. If we use the spectral decomposition with $p_n = g(E_F)^{-1} \delta(E_n - E_F)$, we get

$$G = \frac{1}{2}g(E_F) \left(\frac{e}{L}\right)^2 \tilde{C}_{vv}(0) = \pi \sum_{nm} \left(\frac{e}{L}\right)^2 |v_{nm}|^2 \delta(E_n - E_F) \delta(E_m - E_n) \quad (799)$$

It is implicit that the delta functions are "broadened" due to the assumed non-adiabaticity of the driving, else we shall get vanishing dissipation. The calculation of G in the adiabatic regime requires a more careful treatment, and possibly goes beyond LRT. As long as the broadening is large compared to the level spacing, but small compared with other energy scales, the result is not too sensitive to the broadening parameter, and small corrections are commonly ignored, unless the ring is very small. Schematically the above expression can be written as

$$G = \pi \hbar g(E_F)^2 \left(\frac{e}{L} \right)^2 \overline{|v_{nm}|^2} = \pi \hbar g(E_F)^2 \overline{|\mathcal{I}_{nm}|^2} \quad (800)$$

where the bar indicates that an average should be taken over the near diagonal matrix elements of the velocity operator near the Fermi energy. A somewhat more fancy way to write the same is

$$G = \pi \text{trace} [\mathcal{I} \delta(E_F - \mathcal{H}) \mathcal{I} \delta(E_F - \mathcal{H})] = \frac{1}{\pi} \text{trace} [\mathcal{I} \text{Im}[G(E_F)] \mathcal{I} \text{Im}[G(E_F)]] \quad (801)$$

where $G = 1/(E - \mathcal{H} + i0)$ is the one-particle retarded Green function. This opens the way to formal calculations that are based on path integral or diagrammatic methods.

For a chaotic ring, the dispersion $\overline{|\mathcal{I}_{nm}|^2}$ of the off-diagonal matrix elements is equal, up to a symmetry factor, to the dispersion of the diagonal matrix elements. Note that $\mathcal{I}_{nn} = -\partial E_n / \partial \Phi$. It is common to use the notation $\phi = (e/\hbar)\Phi$. Hence one obtains the Thouless relation:

$$G^{[N]} = \text{factor} \times \frac{e^2}{\hbar} \times \frac{1}{\Delta^2} \overline{\left| \frac{\partial E_n}{\partial \phi} \right|^2} \quad (802)$$

where the numerical factor depends on symmetry considerations, and Δ is the mean level spacing at the Fermi energy. There is a more refined relation by Kohn. The Thouless relation is a useful starting point for the formulation of the scaling theory for localization.

===== [19.4] Conductivity and Conductance

Consider a ring geometry, and assume that the current is driven by the flux Φ . In order to have a better defined model we should specify what is the vector potential $\mathcal{A}(\mathbf{r})$ along the ring. We can regard the values of \mathcal{A} at different points in space as independent parameters (think of tight binding model). Their sum (meaning $\oint \mathcal{A}(\mathbf{r}) \cdot d\mathbf{r}$) should be Φ . So we have to know how Φ is "distributed" along the ring. This is not just a matter of "gauge choice" because the electric field $\mathcal{E}(\mathbf{r}) = -\dot{\mathcal{A}}(\mathbf{r})$ is a gauge invariant quantity. So we have to know how the voltage is distributed along the ring. However, as we explain below, in linear response theory this information is not really required. Any voltage distribution that results in the same electro-motive force, will create the same current.

In linear response theory the current is proportional to the rate in which the parameters are being changed in time. Regarding the values of \mathcal{A} at different points in space as independent parameters, linear response theory postulates a linear relation between $\langle J(\mathbf{r}) \rangle$ and $\mathcal{E}(\mathbf{r}')$ that involves the conductivity matrix $\sigma(\mathbf{r}, \mathbf{r}')$ as a kernel. The current density has to satisfy the continuity equation $\nabla \cdot \langle J(\mathbf{r}) \rangle = 0$. From here it follows that if we replace \mathcal{A} by $\mathcal{A} + \nabla \Lambda(\mathbf{r})$, then after integration by parts we shall get the same current. This proves that within linear response theory the current should depend only on the electromotive force $-\dot{\Phi}$, and not on the way in which the voltage is distributed. Note that $\mathcal{A} \mapsto \mathcal{A} + \nabla \Lambda(\mathbf{r})$ is not merely a gauge change: A gauge transformation of time dependent field requires a compensating replacement of the scalar potential (which is not the case here).

In the following it is convenient to think of a device which is composed of "quantum dot" with two long leads, and to assume that the two leads are connected together as to form a ring. We shall use the notation $\mathbf{r} = (\mathbf{r}, s)$, where \mathbf{r} is the coordinate along the ring, and s is a transverse coordinate. In particular we shall distinguish a left "section" $\mathbf{r} = \mathbf{r}_B$ and a right section $\mathbf{r} = \mathbf{r}_A$ of the two leads, and we shall assume that the dot region is described by a scattering matrix S_{ab} .

We further assume that all the voltage drop is concentrated across the section $\mathbf{r} = \mathbf{r}_B$, and we measure the current \mathcal{I}_A through the section $\mathbf{r} = \mathbf{r}_A$. With these assumptions we have two pairs of conjugate variables, which are (Φ_A, \mathcal{I}_A) and

(Φ_B, \mathcal{I}_B) . Note that the explicit expression for the current operator is simply

$$\mathcal{I}_A = e \frac{1}{2} (v \delta(\mathbf{r} - \mathbf{r}_A) + \delta(\mathbf{r} - \mathbf{r}_A) v) \quad (803)$$

where v is the \mathbf{r} component of the velocity operator. We are interested in calculating the conductance, as defined through the linear response relation $\langle \mathcal{I}_A \rangle = -G^{AB} \Phi_B$. The Kubo expression takes the form

$$G^{AB} = \frac{\hbar}{\pi} \text{trace} [\mathcal{I}_A \text{Im}[G] \mathcal{I}_B \text{Im}[G]] \quad (804)$$

This is yet another version of the Kubo formula. Its advantage is that the calculation of the trace involves integration that is effectively restricted to two planes, whereas the standard version (previous section) requires a double integration over the whole "bulk".

===== [19.5] From the Kubo formula to the Landauer formula

Before we go on we recall that it is implicit that for finite system $\text{Im}[G]$ should be "smeared". In the dot-leads setup which is described above, this smearing can be achieved by assuming very long leads, and then simply "cutting" them apart. The outcome of this procedure is that G^\pm is the Green function of an open system with outgoing wave (ingoing wave) boundary conditions. As customary we use a radial coordinate in order to specify locations along the lead, namely $\mathbf{r} = \mathbf{r}_a(r)$, with $0 < r < \infty$. We also define the channel basis as

$$\langle \mathbf{r}, s | a, r \rangle = \chi_a(s) \delta(\mathbf{r} - \mathbf{r}_a(r)) \quad (805)$$

The wavefunction in the lead regions can be expanded as follows:

$$|\Psi\rangle = \sum_{a,r} (C_{a,+} e^{ik_a r} + C_{a,-} e^{-ik_a r}) |a, r\rangle \quad (806)$$

We define projectors P^+ and P^- that project out of the lead wavefunction the outgoing and the ingoing parts respectfully. It follows that $P^+ G^+ = G^+$, and that $P^- G^+ = 0$, and that $G^- P^- = 0$ etc. We define the operator

$$\Gamma_A = \sum_{a \in A} |a, r_A\rangle \hbar v_a \langle a, r_A| \quad (807)$$

$$= \delta(r - r_A) \otimes \sum_{a \in A} |a\rangle \hbar v_a \langle a| \quad (808)$$

where $v_a = (\hbar k_a / \text{mass})$ is the velocity in channel a . The matrix elements of the second term in Eq.(808) are

$$\Gamma_A(s, s') = \sum_{a \in A} \chi_a(s) \hbar v_a \chi_a^*(s') \quad (809)$$

The operator Γ_B is similarly defined for the other lead. Note that these operators commute with the projectors P^\pm . It is not difficult to realize that the current operators can be written as

$$I_A = (e/\hbar) [-P^+ \Gamma_A P^+ + P^- \Gamma_A P^-] \quad (810)$$

$$I_B = (e/\hbar) [+P^+ \Gamma_B P^+ - P^- \Gamma_B P^-] \quad (811)$$

Upon substitution only two (equal) terms survive leading to the following version of Kubo formula:

$$G^{BA} = \frac{e^2}{2\pi\hbar} \text{trace} [\Gamma_B G^+ \Gamma_A G^-] \quad (812)$$

There is a well known expression (Fisher-Lee) that relates the Green function between plane A and plane B to the S matrix. Namely:

$$G^+(s_B, s_A) = -i \sum_{a,b} \chi_b(s_B) \frac{1}{\sqrt{\hbar v_b}} S_{ba} \frac{1}{\sqrt{\hbar v_a}} \chi_a^*(s_A) \quad (813)$$

Upon substitution we get

$$G^{BA} = \frac{e^2}{2\pi\hbar} \sum_{a \in A} \sum_{b \in B} |S_{ba}|^2 \quad (814)$$

This is the Landauer formula. Note that the sum gives the total transmission of all the open channels.

===== [19.6] From the Kubo formula to the BPT formula

It should be emphasized that the original derivations of the Landauer and the BPT formulas are based on a scattering formalism which strictly applies only in case of an open system (= system with leads which are connected to reservoirs). In contrast to that Kubo formula is derived for a closed system. However, it can be shown that by taking an appropriate limit it is possible to get the BPT formula from the Kubo formula. Namely,

$$\eta^{kj} = \frac{\hbar}{\pi} \text{trace} [F^k \text{Im}[G^+] F^j \text{Im}[G^+]] \quad (815)$$

$$= \frac{\hbar}{4\pi} \text{trace} \left[\frac{\partial S^\dagger}{\partial x_i} \frac{\partial S}{\partial x_j} \right] \quad (816)$$

$$B^{3j} = -\frac{i\hbar}{2\pi} \text{trace} [F^3 (G^+ + G^-) F^j \text{Im}[G^+]] \quad (817)$$

$$= \frac{e}{4\pi i} \text{trace} \left[P_\Lambda \left(\frac{\partial S}{\partial x_j} S^\dagger - \frac{\partial S^\dagger}{\partial x_j} S \right) \right] + \text{intrf} \quad (818)$$

So the sum is

$$G^{3j} = \frac{e}{2\pi i} \text{trace} \left(P_\Lambda \frac{\partial S}{\partial x_j} S^\dagger \right) \quad (819)$$

For more details see Phys. Rev. B **68**, 201303(R) (2003).

[20] Irreversibility and Nonequilibrium processes

===== [20.1] The origin of irreversibility

Assume an isolated system with Hamiltonian $\mathcal{H}(X)$, where X is a set of control parameters that determine the “fields”. For simplicity assume that at $t = 0$ the system is in a stationary state. A driving process means that $X = X(t)$ is changed in time. In particular a cycle means that $X(t_{\text{final}}) = X(t=0)$. A driving process is called *reversible* if we can undo it. In the latter case the combined process (including the “undo”) is a closed cycle, such that at the end of the cycle the system is back in its initial state. Generally speaking a driving cycle becomes reversible only in the adiabatic limit. Otherwise it is irreversible.

Micro-reversibility.— One should not confuse reversibility with micro-reversibility. The latter term implies that the mechanical evolution has time reversal symmetry (TRS). This TRS implies that if we could reverse that state of the system at some moment (and also the magnetic field if exists) then ideally the system would come back to its initial state. This is called Lodschmit Echo. In general it is impossible to reverse the state of the system, and therefore in general micro-reversibility does not imply reversibility!

Sudden process.— The irreversibility of typical systems is related to *chaos*. The simplest example is free expansion. In this example X is the location of a piston. At $t = 0$ the system is prepared in an ergodic state, say a microcanonical state on the energy surface $\mathcal{H}(X_A) = E$. The piston is moved outwards abruptly from X_A to X_B . After some time of ergodization the system will become ergodic on $\mathcal{H}(X_B) = E$. There is no way to reverse this process.

Slow driving.— The more interesting scenario is a slow cycle. Using the assumption of chaos it can be argued that at the end of the cycle the state will occupy a shell around $\mathcal{H}(X_A) = E$. If the system is driven periodically (many cycles), the thickness of this shell grows like $\sqrt{D_E t}$ with $D_E \propto \dot{X}^2$. This diffusion in energy space implies (with some further argumentation) monotonic increase of the average energy. Thus irreversibility implies dissipation of energy: The system is heated up on the expense of the work which is being done by the driving source.

Non equilibrium steady state.— Another reason for irreversibility is having a “frustrated” system that is connected to several baths, each in different temperature, as in the prototype problem of heat conduction. Typically, after a transient, a steady state is reached. But this steady state is not a canonical thermal equilibrium state. With such configuration one can associate a rate of “entropy production”.

===== [20.2] The Boltzmann version of the second law

There are two possible approaches to discuss irreversible processes. One approach, following Boltzmann, is based on the theory of ergodic motion, while the other is the thermodynamic formulation. The Boltzmann approach is based on a statistical definition of entropy. In order to avoid confusion we distinguish between Shanon entropy, Von-Neumann entropy, Boltzmann entropy and Thermodynamic entropy. All except the latter are defined by the same look alike formula $S = -\sum_r p_r \log(p_r)$, but the context and the meaning of the p_r is in general not the same.

Information entropy.— If we have a probability distribution $\{p_r\}$ then S provides a measure for the *uncertainty* which is involved in our knowledge of the statistical state. This point of view that regards S as an information measure has been promoted by Shanon. In the quantum mechanical context we define “classical state” as implying 100% certainty for *any* measurement. Such states do not exist in Nature. Rather the states of minimum uncertainty in N dimensional Hilbert space are the pure states, and they have finite information entropy. See <http://arxiv.org/abs/quant-ph/0401021>. They should be contrasted with the worst mixed state whose entropy is $S = \log(N)$.

Von-Neumann entropy.— Von-Neumann has used a Shanon look-alike formula in order to characterize the *purity* of a quantum state. In the Von-Neumann definition, the p_r are the weights of the pure states in the mixture. It is important to realize that the Von-Neumann entropy has nothing to do with the theory of irreversibility. If we consider for example the free expansion of a wavepacket in a big chaotic box, then we have $S = 0$ at any moment. Still it is nice that the Von-Newman entropy of a canonical state coincides with the thermodynamic definition.

Boltzmann entropy.— Boltzmann has defined S in a way that allows to discuss irreversibility. The idea was to divide the phase space of a system into small cells, and to characterize the statistical state in this representation using S . Then Boltzmann has proposed that S has the tendency to increase with time if the motion is chaotic (a

variation of this idea is the “H theorem” that refers to the reduced one-particle description of a gas particle). The same reasoning can be carried out in the quantum mechanical context where the division of Hilbert space into “cells” is defined by a complete set of projectors. Obviously in the latter context recurrences imply that the dynamics of a quantized closed chaotic system looks irreversible only for a limited time.

State space:— The following visualization is useful. Any canonical state ρ of the system can be represented as a point in a (X, T) plane. We add a vertical axis for the energy. Hence in this extended representation the canonical states form a surface. We refer to this surface as the floor. Non-canonical states with the *same* entropy as the canonical state have a higher energy and accordingly are represented by points *above* the floor. In this space we can define adiabatic surfaces, that consist of states that have the same entropy.

Thermodynamic process:— We visualize a thermodynamic process as a trajectory in the (X, T, E) space. A reversible quasi-static process is represented by a solid line that connects points A and B on the floor. An actual non-reversible process is represented by a dashed line that resides “above” the floor. Of particular interest are processes that start and end at the floor. According to Boltzmann the entropy during a process always increases. Loosely speaking this means that the probability at the end of the process is scattered on more “energy levels”.

===== [20.3] The thermodynamics version of the second law

The Boltzmann entropy is a theoretical construct and hence the statistical version of the second law has no practical value. We have to “translate” both the definition of entropy and the “second law” into a thermodynamic language.

Let us first discuss how define the “entropy” without relaying on Boltzmann. The first step is to characterize any thermal state by empirical temperature θ . This is well defined by the “zeroth law” of thermodynamics. The second step is to represent all the thermal states as points in a $\mathbf{X} = (X, \theta)$ space. Now we can define “adiabatic surface” as the set of states that can be reached via a reversible adiabatic process that does not involve exchange of energy with the environment. We can label each surface by an number $S(\mathbf{X})$, that we call “entropy” (with quotations marks). The convention would be that $S[A] < S[B]$ if we can get from A to B via an irreversible process.

If we have a reversible process that starts at point \mathbf{X} , and ends at point $\mathbf{X} + d\mathbf{X}$ the change in “entropy” is $dS = \nabla S \cdot d\mathbf{X}$. At the same time we can write for the heat $dQ = \mathbf{F} \cdot d\mathbf{X}$. By definition both $dS = 0$ and $dQ = 0$ define the same adiabatic surfaces. It follows that there is an “integration factor” such that $\mathbf{F} = T(X, \theta) \nabla S$. We now postulate that there is a possibility to define S such that T is a function of θ alone. This leads to the definition of “absolute temperature” and “thermodynamics entropy” without the use to relay on Boltzmann.

Let us rephrase the thermodynamic postulate in a more illuminating way. Consider an isothermal process at temperature θ_H that connects two adiabatic surfaces. Consider a second isothermal process at temperature θ_C that connects the same surfaces. To say that dQ has an integration factor that depends on θ alone means that the ratio dQ_H/dQ_C depends only on the temperatures θ_H and θ_C . Hence we can define “absolute temperature” using the definition of Carnot. This also fix the definition of S up to a constant.

The connection with the canonical formalism is quite transparent. Using ideal gas thermometer we have identified $\theta = 1/\beta$, and then we showed that $dQ = \sum_r dp_r E_r$ has an integration factor $T = 1/\beta$ as postulated in thermodynamics. During a reversible quasi-static process the change of the entropy of a system a is $\int dQ_a/T_a$, while that of a second system is $\int dQ_b/T_b$. If we have $T_a = T_b = \theta$, it follows that the total entropy change has an additive property, hence entropy is an extensive quantity.

===== [20.4] The Clausius version of the second law

The Boltzmann-Gibbs entropy is defined as $S = -\sum_r p_r \ln p_r$, where p_r is the probability to be in the r th cell in phase space. The Boltzmann version of the second law states that after any process from state “A” to state “B”

$$S^{universe}[B] - S^{universe}[A] > 0 \quad (820)$$

In order to translate this microscopic formulation into the practical language of thermodynamics one assumes: **(1)** In the initial and final states the system is in equilibrium with bodies that have well defined temperatures T_A and T_B respectively; **(2)** During the process the system absorbs heat from equilibrated bodies that have well defined temperatures, while the system itself might be out of equilibrium; **(3)** The change in the entropy of an equilibrated

body that has a well defined temperature T is $-dQ/T$, where dQ is the heat transfer with the usual sign convention. With these assumptions we get the thermodynamic version of the second law:

$$\left[S^{sys}[B] - S^{sys}[A] \right] - \int_A^B \frac{dQ}{T_{baths}} > 0 \quad (821)$$

In particular for a closed cycle we get the Clausius inequality

$$\text{Entropy production} \equiv - \oint \frac{dQ}{T_{baths}} > 0 \quad (822)$$

Kelvin statement:— The immediate implication of the Clausius inequality is that there exist no process whose sole result is to transfer heat into work. If such process existed one would have $dQ \geq 0$ at any stage of the cycle and hence the total entropy of the universe would decrease. Also the inverse statement is true: if it were possible to devise a machine that violates Clausius inequality, then it would be possible to violate Kelvin's statement. The proof is based on the possibility to combine such a device with a Carnot engine.

Direction of heat flow:— The next simplest application of the Clausius inequality is related to a cycle $(AB)^\#$ in which the system is in contact with T_A , and later in contact with T_B (work is not involved). The result of such cycle is the transfer of an amount q of energy from T_A to T_B . Assuming $T_B < T_A$ it follows from the Clausius inequality that q must be positive, which loosely speaking means that heat can flow only from the high to the low temperature.

Maximum work principle:— Consider an isothermal process. We use the standard assumptions: the temperature of the bath is T_0 , the initial state is equilibrium, and also at the end of the process we wait until an equilibrium is reached. Using the first law of thermodynamics (energy conservation) we can substitute $Q = W + (E(B) - E(A))$, where W is *defined* through this expression as the work done by the system. Using $F(A) = E(A) - T_0 S(A)$ and $F(B) = E(B) - T_0 S(B)$ we get from the second law

$$\text{Work done by the system} = W < F(A) - F(B) \quad (823)$$

Obviously in order to extract "positive" work we need $F(A) > F(B)$. The *maximum* work that can be extracted is equal to the free energy difference. A trivial implication is that if the universe included only one bath with one temperature, it would not be possible to extract work from a closed cycle.

Irreversible work:— In practice, assuming that the state of the system is canonical-like at any instant of time, with a well define temperature T_{sys} at any moment along the $A \mapsto B$ process, we can calculate the change in the entropy of the system as an integral over $dS^{sys} = (dQ + d\mathcal{W}_{\text{irreversible}})/T_{sys}$, leading to

$$\int_A^B \frac{d\mathcal{W}_{\text{irreversible}}}{T_{sys}} + \int_A^B \left(\frac{1}{T_{sys}} - \frac{1}{T_{baths}} \right) dQ > 0 \quad (824)$$

We see that the origin of irreversibility is (i) irreversible work, e.g. frictional effects; (ii) temperature difference between the system and the bath during heat conduction. Additionally, based on the same expression for dS^{sys} , we can write

$$\sum_r dp_r E_r = \int_A^B T_{sys} dS^{sys} = Q + \mathcal{W}_{\text{irreversible}} \quad (825)$$

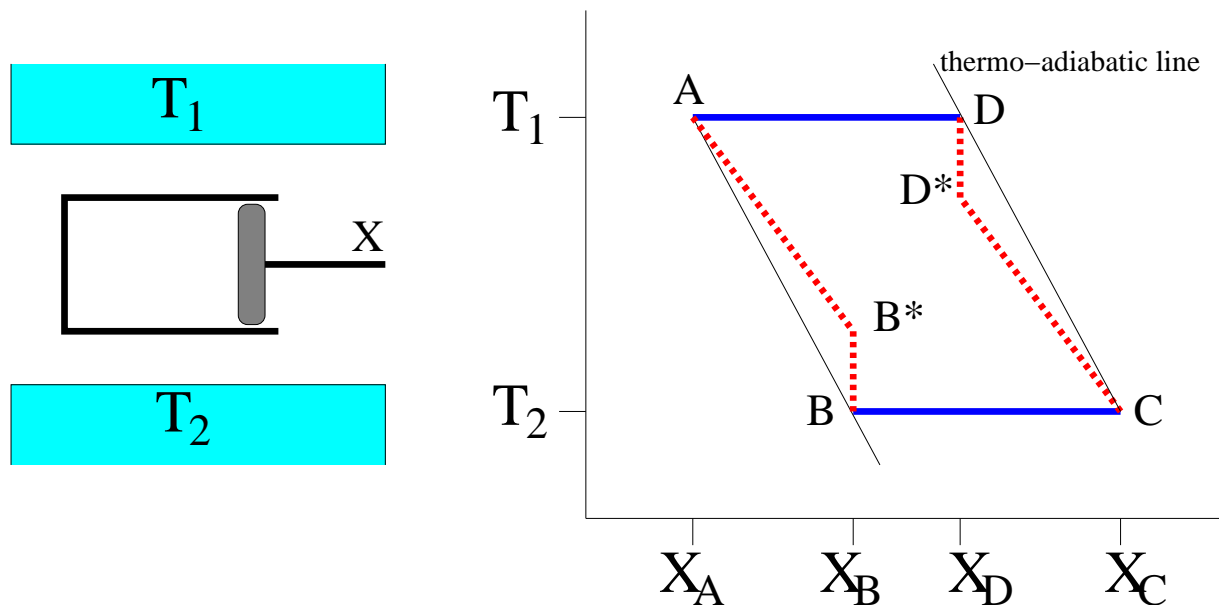
This is the change in the energy which is resulted from transitions between levels. These transitions are induced by the coupling to the environment and/or by the non-adiabaticity of the driving. It is complementary to the reversible work which is obtained from integrating $dW = ydX$ along the $A \mapsto B$ process.

[20.5] The Carnot Cycle paradigm

A *strict adiabatic process* is a quasi-static process during which the system is totally isolated from the environment. For such process we have the adiabatic theorem. Namely, assuming that the motion is chaotic the system that has been prepared with definite energy E will remain on the the same adiabatic surface (classical version) or in the same energy level (quantum version) if a parameter X is being changed very slowly. If the system is prepared with probability p_n in some energy shell (classical) or energy level (quantum) then this probability will not change during the process, and hence also the entropy will remain constant. In the classical version n is the phase space volume of the evolving energy surface, while in the quantum mechanical formulation it is the index that labels the energy levels. In the classical limit $n \in [0, \infty]$, and the associated energy is denoted as $E_n(X)$.

We can represent all the possible *canonical* states of a system as points in (X, T) space. The thermo-adiabatic lines connects points that have the same entropy. A *thermo-adiabatic process* is defined as a quasi-static process along a thermo-adiabatic line. We can think of such process as composed of many infinitesimal steps, where each step consists of a strict adiabatic process followed by a contact interaction with a bath that has the appropriate temperature. To see that the quasi-static limit exists, note the following: If a system is prepared in a canonical state $E_n(X_0)$, Then its energy after a strict adiabatic process is $E^* > E_n(X)$ for any X away from X_0 . For a small variation dX the energy difference can be expanded as $dE^* \propto dX^2$. If after such a variation the system is connected to a bath that has the appropriate temperature, it would relax to a canonical state with the same entropy. This relaxation involves an entropy production $dS = dE^*/T$. Integrating dS over the whole process we see that in the quasi-static limit the entropy production is zero.

A strict Carnot cycle involves only two heat baths. The cycle (ABB^*CDD^*) is illustrated in the Figure. The initial preparation is canonical at $A(T_1, X_A)$. The process from $A(T_1, X_A)$ to $B^*(X_B)$ is *strictly* adiabatic. At the end of this stage the obtained state is not canonical. The process from $B^*(X_B)$ to $B(X_B, T_2)$ is the equilibration due to contact with a bath that has the temperature T_2 . It is an irreversible relaxation process in which the system goes to a lower energy with the same entropy. At the end of this process the obtained state is canonical. The process form $B(X_B, T_2)$ to $C(X_C, T_2)$ is quasi-static in *contact* with the same heat bath. The process from $C(X_C, T_2)$ to $D^*(X_D)$ is *strictly* adiabatic. The process from $D^*(X_D)$ to $D(X_D, T_1)$ and later back to $A(T_1, X_A)$ is in contact with the heat bath T_1 .



===== [20.6] Fluctuations away from equilibrium

It is customary to say that at equilibrium the expectation value of an observable reflects the typical value of this observable, while the fluctuations are relatively small. If the central limit theorem applies the RMS/mean should scale as $1/\sqrt{N}$. However, we may insist to study the statistics of the tails. These might reveal interesting information about the underlying dynamics.

If a system, that has a constant density of states, were isolated, then it would be natural to expect that the distribution function of quantities like work and entropy production would be symmetric: $P(-s) = P(s)$. But in the thermodynamic context it is more likely to have

$$P(-s) = e^{-\beta s} P(s), \quad [\beta\text{-symmetric distribution}] \quad (826)$$

It follows that $P(s)$ can be written as a product of a symmetric function and an exponential factor $e^{\beta s/2}$. Another consequence of the β -symmetry is

$$\langle e^{-\beta s} \rangle = 1, \quad [\text{convex average}] \quad (827)$$

The latter equality can be re-phrased as follows: In analogy with the definition of *harmonic* average and *geometric* average that are defined as the inverse of $\langle (1/s) \rangle$ and as the exp of $\langle \log(s) \rangle$ respectively, here we can define a *convex* average that is defined as the log of the above expression. The convex average is zero for a β -symmetric distribution, while the standard algebraic average is positive

$$\langle s \rangle > 0, \quad [\text{convex inequality}] \quad (828)$$

While for a symmetric distribution the average value $\langle s \rangle$ has to be zero, this is no longer true for a β -symmetric distribution. Rather the average should be related to the variance. If we assume that s has Gaussian distribution with average value $\langle s \rangle = \mu$ and variance $\text{Var}(s) = \sigma^2$, then β -symmetry requires

$$\langle s \rangle = \frac{1}{2} \beta \text{Var}(s), \quad [“\text{fluctuation dissipation}” \text{ relation}] \quad (829)$$

This is like a fluctuation dissipation relation. We can formalize this relation for non-Gaussian distribution in terms of cumulant generating function $g(\lambda)$ which is defined through

$$\langle e^{-\lambda s} \rangle \equiv e^{g(\lambda)} \quad (830)$$

Note that due to normalization $g(0) = 0$, while $g'(0) = -\mu$ and $g''(0) = \sigma^2$. In particular for a Gaussian $g(\lambda) = -\mu\lambda + (1/2)\sigma^2\lambda^2$. For a symmetric distribution $g(-\lambda) = g(\lambda)$. But for β -symmetry we must have

$$g(\beta - \lambda) = g(\lambda), \quad [\text{characterization of } \beta\text{-symmetric distribution}] \quad (831)$$

Again we see that for a Gaussian β -symmetry implies a relation between the mean and the variance.

===== [20.7] The Crooks relation and Jarzynski equality

The Crooks relation and Jarzynski equality regards the probability distribution of *work* done during a non-equilibrium process that connects canonical states A and B .

Let us have in mind a gas in cylinder with a movable piston. Initially the piston is in position A , and the gas in equilibrium with temperature T_0 . The canonical probabilities are

$$p_r(A) = \frac{1}{Z(A)} e^{-\beta E_r(A)} = \exp \left[-\frac{E_r(A) - F(A)}{T_0} \right] \quad (832)$$

Now we displace the piston to position B doing work \mathcal{W} . After that we can optionally allow the system to relax to the bath temperature T_0 , but this no longer affects \mathcal{W} . The distribution of work is defines as

$$P(\mathcal{W}) = \sum_r p_r(A) \delta(\mathcal{W} - (E_r(B) - E_r(A))) \quad (833)$$

It is implicit here that we assume a conservative system with a well-defined invariant measure that allows division of phase space into "cells". The states $E_r(B)$ are associated with $E_r(A)$ through the dynamics in a one-to-one manner. Note that if the dynamics is non-adiabatic the order of the cells in energy space is likely to be scrambled. It follows from the above definition that

$$\left\langle \exp \left[-\frac{\mathcal{W}}{T_0} \right] \right\rangle = \frac{1}{Z(A)} \sum_r e^{-(1/T_0)E_r(A)} \exp \left[-\frac{E_r(B) - E_r(A)}{T_0} \right] = \exp \left[-\frac{F(B) - F(A)}{T_0} \right] \quad (834)$$

This is the Jarzynski equality. It can be regarded as a refinement of the inequality $\mathcal{W} > (F(B) - F(A))$, and it reduces to $\mathcal{W} = (F(B) - F(A))$ in the the case of a quasi-static adiabatic process.

Crooks relation.— The Jarzynski equality can be regarded as the outcome of the Crooks relation. We can define a probability distribution $P_{rev}(\mathcal{W})$ for a process that starts with a canonical state B , in complete analogy with the definition of $P(\mathcal{W})$. Now the probabilities $p_r(A)$ are replaced by $p_r(B)$. It follows that

$$P_{rev}(-\mathcal{W}) = \exp \left[-\frac{\mathcal{W} - (F(B) - F(A))}{T_0} \right] P(\mathcal{W}) \quad (835)$$

The Jarzynski equality follows if we integrate both sides over \mathcal{W} . In the standard references the phrasing of the Crooks relation is a somewhat more involved. One defines a *joint* probability distribution

$$P(E_b, E_a) = \sum_r p_r(A) \delta(E_a - E_r(A)) \delta(E_b - E_r(B)) \quad (836)$$

and the statement becomes

$$\frac{P(E + \mathcal{W}, E)}{P_{rev}(E, E + \mathcal{W})} = \exp \left[\frac{\mathcal{W} - (F(B) - F(A))}{T_0} \right] \quad (837)$$

The visualization of this inequality is as follows: Define the *source* as a shell of thickness dE_a around $E_a = E$, and the *destination* as a shell with thickness dE_b around $E_b = E + \mathcal{W}$. Denote by $N \propto dE_a dE_b$ the number of cells that are connected by the dynamics. The probability to observe a process from E_a to E_b is $N p_r(A)$. The probability to observe an analogous reversed process is $N p_r(B)$. The ratio is $p_r(A)/p_r(B)$, leading to the Crooks relation. Finally we note that in the quantum context the object that corresponds to $P(\mathcal{W})$ is

$$P_{A \rightsquigarrow B}(\omega) = \sum_{n,m} p_n(A) \left| \langle m(B) | U(t) | n(A) \rangle \right|^2 \delta(\omega - (E_m(B) - E_n(A))) \quad (838)$$

where $U(t)$ is the evolution operator. The Crooks relation in this context can be regarded as a straightforward variation on the derivation of the "detailed balance relation" that applies to a spectral functions $\tilde{S}(\omega)$.

The FD relation.— Let us see what is the implication on the Crooks relation with regard to a simple closed cycle for which $F(B) = F(A)$. In such case $P(\mathcal{W})$ is a β -symmetric distribution. It follows that there is a "fluctuation dissipation relation"

$$\langle \mathcal{W} \rangle = \frac{1}{2T} \text{Var}(\mathcal{W}) \quad (839)$$

Considering a multi-cycle process $\text{Var}(\mathcal{W}) = 2D_E t$ and $\langle \mathcal{W} \rangle = \dot{\mathcal{W}} t$, leading to the dissipation-diffusion relation that we have derived in past lecture $\dot{\mathcal{W}} = (1/T)D_E$, from which follows the dissipation-fluctuation relation $\eta = \nu/(2T)$.

===== [20.8] The nonequilibrium fluctuation theorem

The nonequilibrium fluctuation theorem (Evans, Cohen, Morris, Searles, Gallavotti) regards the probability distribution of the *entropy production* during a general non-equilibrium process.

The clearest formulation of this idea assumes that the dynamics is described by a rate equation. The transition rates between state n and state m satisfies

$$\frac{w(n|m)}{w(m|n)} = \exp \left[\frac{E_m - E_n}{T_{nm}} \right] \quad (840)$$

Where T_{nm} is the temperature that controls the nm transition. We can regard the rate equation as describing a random walk process. Consider a trajectory $x(t)$. If the particle makes a transition from m to n the entropy production is $(E_m - E_n)/T_{nm}$. Accordingly

$$\frac{P[x(t)]}{P[x(-t)]} = \exp [\Delta S[x]] \quad (841)$$

As an example for the practicality of this relation consider the current fluctuations in a ring. The fluctuation theorem implies that the ratio $P(I)/P(-I)$ at non-equilibrium steady state should equal the above Boltzmann factor, where $S[x]$ is the entropy production due to a particle that encircles the ring.

Heat conduction.— A prototype application of the above relation is to the analysis of heat flow from hot bath T_H to cold bath T_C . The temperature difference is $\epsilon = T_H - T_C$. We assume that the conductor that connects the two baths can be modeled using a master equation. The transition between states of the conductor are induced by the bath and are like a random walk. With any trajectory we can associate quantities Q_H and Q_C that represent that heat flow from the baths into the conductor. From the fluctuation theorem it follows that

$$\frac{P(Q_H, Q_C)}{P(-Q_H, -Q_C)} = \exp \left[-\frac{Q_C}{T_C} - \frac{Q_H}{T_H} \right] \quad (842)$$

Next we define the absorbed energy $\bar{Q} = Q_H + Q_C$ and the heat flow $Q = (Q_H - Q_C)/2$. We realize that in the long time limit $Q \sim t$ while the fluctuations of \bar{Q} are bounded. Accordingly we get

$$\frac{P(Q)}{P(-Q)} = \exp \left[\left(\frac{1}{T_C} - \frac{1}{T_H} \right) Q \right] \quad (843)$$

If we use a Gaussian approximation, we get a "fluctuation-dissipation" relation

$$\langle Q \rangle = \frac{1}{2} \left(\frac{1}{T_C} - \frac{1}{T_H} \right) \text{Var}(Q) \quad (844)$$

The relation can be linearized with respect to $\epsilon = T_H - T_C$. The thermal conductance is defined through $\langle Q \rangle = K\epsilon \times t$, and the intensity of fluctuations through $\text{Var}(Q) = \nu \times t$. Thus we deduce that

$$\langle \dot{Q} \rangle = K \times (T_H - T_C), \quad \text{with } K = \frac{1}{2T^2} \nu \quad (845)$$

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